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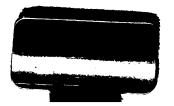
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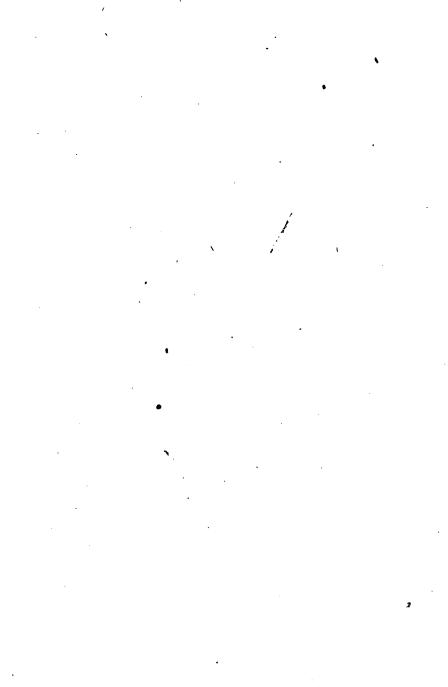
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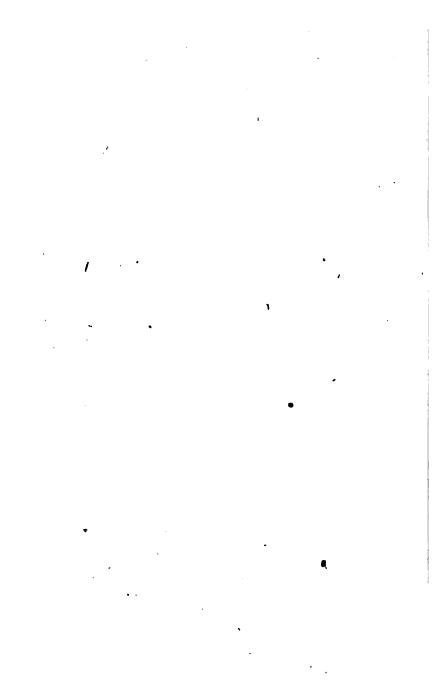
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BOILER FEED WATER

A CONCISE HANDBOOK OF WATER FOR BOILER FEEDING PURPOSES

(ITS EFFECTS, TREATMENT, AND ANALYSIS)

BY

PERCY G. JACKSON, F.I.C.

FORMERLY CHEMIST TO THE NATIONAL BOILER AND GENERAL INSURANCE COMPANY, LIMITED



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PREFACE

So far as I am aware no book on the subject of Boiler Feed Water has hitherto been written by any one having extensive experience as chemist to a boiler insurance company, and I feel that an intimate practical knowledge of the subject cannot otherwise be so well obtained.

The investigation of occasional isolated cases of feed-water trouble is undoubtedly very useful, and much helpful information is thus obtained, though it can hardly be expected to yield the same general knowledge of the subject as that resulting from the consideration of analyses in conjunction with the history of the boilers, or the batteries of boilers concerned, though I am well aware that even then there are many possible factors which are not thus disclosed. Slight variations in the working conditions, which may not even be brought to notice by a special investigation of a particular case, can yet have an important bearing on the subject, especially in those instances where one or more boilers in a battery are affected, while the others are in a satisfactory condition.

Makers of water softening plants have not usually the expert chemical staff necessary thoroughly to investigate troubles which continue even after their plants have been put to work, nor should they be (although they usually are) expected to render continued and expensive services gratis, after having put down a plant which is capable of doing its work efficiently. Some of them do keep in touch with their plants for a long time, and offer regular advice as to necessary changes in the treatment as judged from log sheets of daily tests made by the users, but beyond this they cannot reasonably be expected to go. If they erect a plant capable of reducing the hardness-forming salts to a minimum, and eliminating oil; and if the plant is so designed and constructed as to continue to work satisfactorily with reasonable attention for a number of years, they may be considered to have fulfilled their obligations, unless, of course, they have given special guarantees to effect specified results.

It is not intended that this book shall explain theoretically why various constituents of feed water cause certain undesirable results, but only how experience has shown that these undesirable results may be eliminated, or at least mitigated.

There is still much to be learnt on the subject, and probably will be until some one comes forward with unlimited time to devote to such matters, and who is unhindered in the thorough prosecution of his researches by financial considerations. He must not expect to carry through the work in a laboratory, but must spend much of his time in the stoke-hole, always observant of details, able to advise slight or important changes in the working conditions, and note the results obtained thereby.

All efforts to fathom boiler feed water troubles are handicapped by the fact that it is impossible to see what is actually happening inside a boiler while it is at work, and by the impossibility of obtaining exact working conditions in laboratory experiments.

This work is the result of the experience largely gained by me while working as chemist to the National Boiler and General Insurance Company, Limited, and I wish to express my indebtedness, for allowing me to publish this book, to the Company, and to Mr. Edward G. Hiller, the chief engineer, and other engineers of his staff, who have, during the years of my service, given me the benefit of their experience.

I trust the information in this book will be found to be reliable, concisely stated, and of practical use.

PERCY G. JACKSON

January 1919

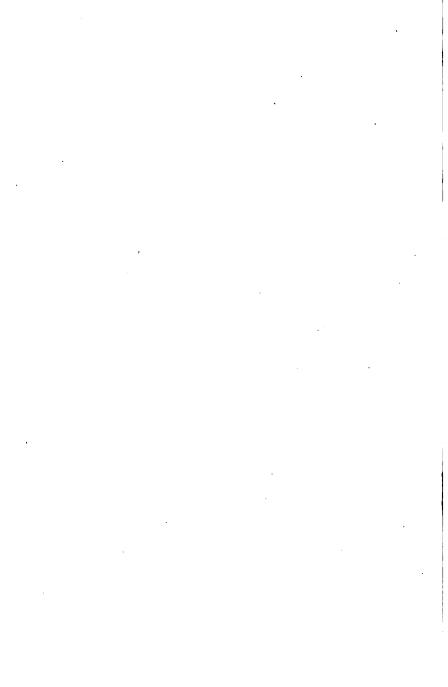
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CHAPTER I

INTRODUCTORY

Perfect boiler feed water can never be obtained from any natural source, and though a small proportion of the available supplies may be considered suitable for use without treatment, most of them require treatment in some way or other if the boilers using them are to be kept as clean and free from corrosion as possible. A few may be non-corrosive, but practically none can be found which do not form more or less deposit in boilers, and as a rule some of the deposit remains on the plates or tubes in the form of scale.

Unsuitable feed water in boilers may cause damage in a number of ways, such as:—

- (a) Corrosion of the plates.
- (b) Corrosion of the fittings.
- (c) Grooving of the angles and seams.
- (d) Leakages, and sometimes shearing off of rivets owing to straining of the seams through excessive expansion and contraction of the plates.
- (e) Bulging, hogging, or ripping of the tubes. Even the shell plates may be bulged.
- (f) Engine troubles due to priming of the water in the boilers.

Corrosion of the plates of a boiler may occur in several forms, of which the principal are:—

(a) Isolated pittings, which may sometimes perforate a plate without materially reducing its strength.

(b) Honeycomb pitting, consisting of areas of close isolated pittings. This is more serious than the above, its importance depending on the size and depth of the pits and the intervals between them.

(c) Confluent pitting, which occurs in areas of varying size and may cause serious weakening of the plates.

(d) Smooth wasting, by which the whole of the original surface of the metal in a particular area is removed, leaving a more or less uniform surface, which may not be readily noticeable. The depth and extent of the wasting thus occurring is often difficult to determine, and serious weakening of the plates may have taken place before it is detected. When suspected it is usually necessary to drill the plate and gauge the remaining thickness.

(e) Grooving in angles and at seams, or at any junction of two plates. This may lead to the formation of cracks,

or even to rupture.

(f) Graphitic wasting of east iron. In this form a portion of the iron is apparently dissolved away, while the remainder is converted into black oxide, which, together with graphite and silica, remain behind in the form of, and similar in appearance to, the original metal, for which it can readily be mistaken. This form usually occurs in economiser pipes.

The causes of corrosion will be dealt with in another chapter.

Leakages, Bulging, etc., are usually caused by overheating of the tubes and plates of boilers mainly owing to scale and deposit, especially when grease is present. Scale in boilers not only retards the passage of heat through the plates or tubes, but also, by keeping the water from direct contact with the metal, may cause it to become more or less overheated, and result in undue strains being set up. It frequently happens, usually when grease is present in the scale, that the overheating is so severe as to lead to softening of the metal and consequent bulging or hogging of the plates or tubes, shearing of rivets and opening of seams, and possibly collapse or rupture. Sometimes portions of tubes may be seriously burnt, presumably by becoming partially emptied of water, the metal then becoming red-hot and combining with the oxygen in the water vapour. Such oxidation or burning may be of considerable depth. Even soft deposit, especially if of a light floury nature, or containing grease, may lead to serious overheating of the metal on which it is deposited, especially if it collects on those parts exposed to the greatest heat of the furnaces.

The overheating of plates caused through scale or deposit sometimes leads to corrosion by bringing about chemical changes in the constituents of the water, which might not have occurred at the lower normal temperature of the plates. Such decomposition will take place in actual contact with the plates, and the corrosive compounds formed, being shielded from the water by the scale, cannot readily be washed away, and may consequently continue their action for some time.

Grease is very objectionable in boilers, not only on account of the overheating troubles it may lead to, but also owing to the possible corrosion it may cause if it contains either animal or vegetable oil. Animal and vegetable oils contain fatty acids in combination with glycerine, and under the conditions which exist in steam boilers the fatty acids may become liberated and attack the plates.

Priming or Foaming is caused by certain constituents in the water in the boiler, especially where the conditions

of working lead to sudden heavy demands on the steam. This trouble will be dealt with in a later chapter.

As previously stated, perfect feed water cannot be obtained from any natural source, and it may be fairly said never to be found at all, unless specially distilled for the purpose in evaporating plants such as are used in marine practice. The distilled water obtained as condensate from surface or other similar condensers always contains grease, and frequently mineral constituents carried over from the boilers in the steam. It is commonly considered that the condensate from steam turbines is free from grease, but in practice it is seldom found to be entirely so. Small quantities of grease, too small to affect the appearance of the water, and which may escape detection by simple tests, can yet have a very decided effect in causing overheating, especially in heavily fired boilers.

Passing greasy steam through oil separators will result in the removal of a large proportion of the grease, but there will always remain traces which cannot be removed by mechanical means.

If surface condenser water only could be used, little harm might result, but it is almost invariably necessary to introduce a certain proportion of make-up water, and this will in all probability contain some scale-forming constituents, which, when precipitated in the boilers, will entangle a portion of the oil, and result in a greasy scale or deposit. It may be thought that if only a small proportion of make-up is needed, or if it contains little scale-forming matter, it will be of no consequence. This is a mistaken idea, as with a given proportion of oil, the less the amount of deposit formed, the larger will be the percentage of oil in it, and its power of preventing the water coming into contact with the plates thereby increased.

It is surprising how little grease may have serious consequences. One part of grease in a thousand parts of scale or deposit may lead to bulging or hogging in heavily fired boilers.

Rain water is often responsible for corrosion in boilers owing to traces of acid gases dissolved from the atmosphere, especially when collected in large towns or manufacturing districts, and it usually contains a certain amount of suspended matter composed of soot and dust. At times rain water contains appreciable quantities of mineral matter in solution even if collected direct into a clean vessel. As much as a hundred degrees of hardness has been found in samples thus carefully collected.

Speaking in general, well waters are usually the most sedimentary, and also more likely to contain corrosive mineral constituents than water obtained from other sources. River waters, as a rule, have less scale-forming salts, and unless polluted are not so likely to be as corrosive as well supplies. Surface waters collected in moorland districts are mostly of a soft nature, but owing to peaty matter which they usually contain, and their comparative freedom from calcium carbonate, may have decided corrosive properties.

The Hardness of water means its power of destroying soap by the displacement of the sodium or potassium of the soap by calcium, magnesium, or other metals, which form insoluble salts with fatty acids and are therefore precipitated.

Throughout this book *Degrees of Hardness* means English degrees—that is, the equivalent in grains per gallon of calcium carbonate of the total calcium and magnesium salts present. Where iron, aluminium, or manganese salts are present in a water, their equivalent

in calcium carbonate should also be included in the *Hardness*, as they too have soap-destroying properties.

The term "Temporary Hardness" was originally applied to that portion of the hardness which was precipitated by boiling. This is principally the carbonates, but as some of the carbonates will still remain in solution after even prolonged boiling, while some of the other salts may be precipitated in addition to carbonates, the hardness thus represented is somewhat indefinite and variable, depending to a certain extent on the exact method of determination, as well as on the other salts present in the water. It is preferable therefore to consider "Temporary Hardness" to be all the hardness present in the form of carbonates, and the term is thus used in this book.

"Permanent Hardness" is used to indicate all hardness present other than as carbonates.

"Alkalinity" is the equivalent, in terms of grains per gallon of calcium carbonate, of those salts which have the power of neutralising acids. This is usually the carbonates, though in waters which have been chemically treated it will include caustic lime and caustic soda if present. It is sometimes referred to as "Degress of Alkalinity" for convenience, as it is comparable with "Degrees of Hardness."

CHAPTER II

MINERAL CONSTITUENTS

Though waters differ widely in constitution, the mineral salts usually present are comparatively few, comprising the carbonates, sulphates, chlorides, and nitrates of calcium, magnesium, and sodium, together with a small proportion of silica. Potassium is probably present as a rule, but it is seldom considered necessary to test for or estimate it, and it is therefore usually included with the sodium salts when reporting results. Some waters also contain appreciable, and occasionally large, quantities of the salts of iron, aluminium, and manganese.

It is usual, when discussing the composition of water, to speak of carbonates, but strictly speaking this is incorrect in most cases. In natural waters carbonates are always present in the form of bicarbonates, which compounds contain twice as much carbonic acid (carbon dioxide) as the carbonates. The additional carbonic acid required to convert carbonates into bicarbonates is only loosely held, as mentioned later, and may be conveniently referred to as "Half-combined Carbonic Acid."

In the following discussion of the chief characteristics of the principal salts, the word "scale" may sometimes be intended to mean any deposit formed in the boilers, whether as actual scale, loose deposit, or mud.

Calcium Carbonate is derived from chalk or limestone and is the most common of all the scale-forming constituents found in waters. It is only sparingly soluble in water except in the form of bicarbonate, in which form, as previously mentioned, it is always found in natural waters. The solubility of the normal carbonate varies according to the nature and amount of other salts present, but it is usually considered to be soluble to the extent of about three grains per gallon in pure cold water. It is difficult to say what is the solubility of the bicarbonate, but twenty to thirty grains per gallon are found fairly frequently in very hard waters. Calcium carbonate is not only non-corrosive in boilers, but it has a tendency to neutralise the corrosive properties of other constituents, owing to its power of neutralising the acid produced by their decomposition.

Calcium bicarbonate is readily decomposed by heat with the liberation of the half-combined carbonic acid, leaving the less soluble carbonate, and this results in its precipitation in boilers. It is similarly precipitated from solution by the addition of lime, which has a great affinity for, and therefore removes, the half-combined carbonic acid. This fact has led to the use of lime for the precipitation of calcium carbonate in softening plants.

Calcium Sulphate, usually derived from gypsum, is frequently present in water. It is fairly freely soluble in cold water, and its solubility increases slightly up to about 100° Fahr., at which temperature it is soluble to the extent of about one hundred and fifty grains per gallon. Above 100° Fahr. the solubility slowly decreases, while above 212° Fahr. it falls off rapidly. The solubility at the working temperature of most boilers is small, and as a result calcium sulphate is thrown out of solution

in a crystalline form, and by itself will usually form a hard scale, somewhat resembling porcelain. On this account, calcium sulphate is a decidedly objectionable constituent in feed waters owing to the difficulty of removing the scale when cleaning the boilers. Calcium sulphate is considered to be an inert salt, and not liable, therefore, to cause corrosion in boilers.

On the addition of sodium carbonate (soda ash), calcium sulphate is precipitated as carbonate, and by this means it is usually removed in softening plants, sodium sulphate remaining in its place. Barium carbonate is occasionally used instead of soda ash for the precipitation of calcium sulphate owing to the fact that the salts resulting from the reaction (calcium carbonate and barium sulphate) are both precipitated, and the calcium sulphate is thus removed without leaving any other salt in its place. Unfortunately barium carbonate is so much more expensive than soda ash that the cost of treatment is usually considered prohibitive, otherwise it might be a most useful reagent in softening plants.

Calcium Chloride is only occasionally found in waters. Being extremely soluble in water at all temperatures, it is never likely to be deposited in boilers. It is a stable compound and not liable, therefore, to cause corrosion directly, but possibly it may interact with magnesium sulphate under suitable conditions, forming magnesium chloride, and thus leading to corrosion.

Calcium chloride is precipitated as carbonate by soda ash, leaving sodium chloride in solution.

Calcium Nitrate is also an extremely soluble salt occasionally present in water and never likely to be deposited in boilers. Like all nitrates it is probably liable to decomposition at high temperatures with the liberation of acid which will readily attack the boiler plates.

Calcium nitrate is precipitated as carbonate by soda ash, leaving sodium nitrate in its place.

Magnesium Carbonate, usually derived from magnesian limestones, is a fairly common constituent in water, and, like the corresponding calcium salt, is always present as bicarbonate. The bicarbonate is much more soluble in water than the carbonate, but even the normal carbonate is fairly soluble, decidedly more so than calcium carbonate. Magnesium carbonate is seldom found in the scale formed in boilers, owing to the fact that under boiler conditions it is almost invariably converted into hydrate. Though probably not directly corrosive, experience appears to show that, similarly to the other magnesium salts which occur in water, magnesium carbonate may interact with chlorides to form corrosive salts.

Like the corresponding calcium salt, magnesium bicarbonate is converted into carbonate by heat, or by treatment with lime. The carbonate is, however, somewhat too soluble in water to be precipitated to any great extent, but if twice as much lime be used as is necessary to remove the half-combined carbonic acid, the additional lime further reacts with the carbonate to form the almost insoluble magnesium hydrate together with calcium carbonate, both of which will be precipitated. Caustic soda will similarly precipitate magnesium hydrate, but in this case sodium carbonate will remain in solution.

Magnesium Sulphate, commonly known as Epsom salts, is found to some extent in most waters. It is a very soluble salt, but not nearly so soluble as the chlorides and nitrates of calcium and magnesium. Owing to its solubility, magnesium sulphate is not precipitated as such in boilers, and is therefore frequently classed as a non-scale-forming constituent. This is usually incorrect, as in practice it is seldom found to accumulate in boilers

to any great extent. This is probably due to the fact that it may react, under boiler conditions, with chlorides and nitrates, the resulting salt being afterwards converted into the insoluble hydrate, and thus precipitated. Though experiments appear to show that magnesium sulphate is not materially corrosive, there is little doubt that in practice it usually reacts as above mentioned and forms corrosive salts, and it may safely be asserted that when a fair quantity of magnesium sulphate is present in conjunction with chlorides and nitrates of other metals, corrosion is likely to result.

Magnesium sulphate is usually removed in softening treatment by means of caustic soda, which precipitates magnesium hydrate, while sodium sulphate remains in solution. As a mixture of soda ash and lime will interact and form caustic soda, this mixture, being quite as effective and decidedly cheaper, is usually used in preference to caustic soda itself.

Magnesium Chloride, Magnesium Nitrate.—These are well known as very objectionable constituents in feed water. They do not usually occur in large proportion, but are frequently found in small quantities. Both are extremely soluble in water and are not, therefore, deposited in their original form, but by decomposition at boiler temperatures they are nearly always converted into the insoluble hydrate which is precipitated, while acids are liberated which readily attack boiler plates.

These constituents are removed in softening plants by caustic soda, or a mixture of lime and soda ash, in the same way as the sulphate.

Ferrous Sulphate (Sulphate of Iron) is the form in which iron usually occurs when present in quantity in water, and though in smaller quantities iron is frequently shown in analyses as carbonate, it is at least doubtful

whether the carbonate is really present in solution as such.

Though sulphate of iron is fairly soluble in water, it usually commences to precipitate as basic carbonate or basic sulphate on exposure to air, especially if carbonates of other metals are present, and this precipitation generally continues until the water has become distinctly acid in reaction, provided sufficient sulphate of iron be present. In boilers, precipitation will take place more quickly, and a scale will be formed consisting of the basic iron salts.

When iron is deposited from water, either hot or cold, acid is liberated, and on this account waters containing it are extremely corrosive when used in boilers, and such waters should be avoided if possible for feeding purposes, and in any case should not be used unless efficiently purified by softening treatment.

Ferrous sulphate is removed in softening plants by caustic soda, or lime and soda ash, in the same way as magnesium salts.

Aluminium Sulphate is not so frequently found in quantity in waters as sulphate of iron, but it is similar to it in most respects, and no less objectionable, having extremely corrosive properties.

Manganese Sulphate is also occasionally present in fair proportion in water. Its effect is difficult to ascertain, as it is seldom, if ever, present except in conjunction with iron or aluminium. Probably it does little harm except to assist in the formation of scale.

Manganese sulphate will be removed in softening plants by the caustic soda, or lime and soda ash treatment.

Silica is usually found only in very small proportion, and is not of much importance, except that it slightly increases the quantity of scale.

The above list comprises all the important scale-forming mineral salts commonly found in water, but the alkali metals, sodium and potassium, are almost invariably present in some form or other, such as bicarbonates, sulphates, chlorides, and nitrates. They never form scale, though very occasionally they may crystallise out in boilers if they are allowed to accumulate to an excessive degree by working the boilers for too long a period between cleaning times, or by failure to make proper use of the blow-off cock for keeping down the density of the water.

In land boilers the saline matter in solution should never be allowed to exceed 5500 grains (12½ ounces) per gallon, which is equivalent to 2½ thirty-seconds when tested by means of a salinometer graduated in accordance with marine practice. It must be clearly understood that working to such a high concentration is not to be recommended, and should only be allowed in special cases where the feed water is of so saline a nature that serious loss of economy, or great inconvenience, would result had the boilers to be emptied frequently.

Generally speaking, the lower the maximum concentration the better. If boilers can be conveniently and economically emptied before 1100 grains per gallon (half a thirty-second) has been exceeded, it will in most cases be wiser to adopt the practice. The higher the concentration in a boiler, the greater will be the liability to undue straining and other overheating troubles, and also to chemical reactions leading to corrosion, especially when nitrates are present in quantity.

Contamination.—In addition to the natural mineral constituents of water there may be certain other constituents present due to pollution, some of which are of

very great importance where the water is to be used in boilers. The principal of these are:—

Ammonium Sulphate, which is fairly frequently found in water, and which usually owes its presence to some contamination from gas purifying plants or coke ovens. It will not form deposit in boilers, but it has virulent corrosive properties due to the readiness with which it dissociates, when in contact with the hot plates of a boiler, with the liberation of sulphuric acid. Boiler plates have been known to be eaten through in a few months by this objectionable compound.

Sulphuric Acid may be run into rivers from the pickling vats used in steel-works, or from other works processes, and should it be present in such quantity as to render the water acid in the vicinity of the boiler feed suction pipe, very serious corrosion may result.

In the case of the discharge from steel-works, the effluent would usually be a solution of sulphate of iron in acid. From explosive works a mixture of nitric and sulphuric acids may be run to waste in such a way as to lead to the pollution of a boiler feed supply.

Picric Acid.—At the present time this chemical, is being found in certain canals and rivers due to effluent from explosive works. So far there has not been any great amount of experience to be gained as to its effect, but there is little room for doubt that it has decidedly corrosive tendencies and should, therefore, be avoided. Picric acid is a powerful yellow dye and its presence in water is readily noticeable owing to its yellow colour, which is quite perceptible even when present in unimportant quantity.

CHAPTER III

CORROSION

THE subject of corrosion is one that has exercised the minds of capable chemists and engineers for many years, some dealing with corrosion of metals in general, while others have confined themselves mainly to the corrosion of iron and steel. Innumerable experiments, many of them very elaborate and ingenious, have been carried out on a laboratory scale, under varying conditions, on different samples of metal, and with aqueous solutions of various salts or mixtures of salts, but unfortunately the results have not usually been very helpful in ascertaining the causes of, or discovering remedies for, the corrosion of boilers.

Generally speaking, it may be said that the only really useful information is that gained by noting the results in practice from the use of waters of known composition, and even then reliable information is difficult to obtain owing to the variations which occur from time to time in the composition of most water supplies, and the great differences in the conditions under which they are used. There is often a doubt whether the effects noted are the result of the water as analysed, or of some temporary changes in composition which may have occurred.

The question as to whether galvanic action is, or is not, the cause of wasting in boilers has often been the subject of discussion, and it is still more or less unsettled. In all probability both the advocates and the opponents of the galvanic theory are more or less right, and we come back to the old question as to which came first, the hen or the egg?

When the constituents of a water, or the products of decomposition, are such as favour corrosion, electric currents are set up in certain parts of the boiler owing to differences in potential, and the result is that those parts which are electro-positive to the others are likely to be attacked and corroded. If the composition of the water did not favour corrosion, then electric currents would not be produced, whereas if the metal of the boiler was of such a uniform character that no difference in potential existed there could be no electric current, and probably no corrosion would take place. It can hardly be disputed that galvanic action does have some influence, as we find so many instances of severe wasting at the junction of dissimilar metals, the metal which is electro-positive being the one attacked, and the wasting being local and close to the point of junction.

It is not even necessary to have a junction of two distinctly different metals in order to obtain differences in potential; two pieces of iron or steel of the same make, and of approximately the same composition, will almost invariably have a slight difference in potential, and even different parts of the same piece may show a difference in potential. Then again, if one part of a piece of metal is subjected to strain, such as that which results from bending, a potential difference is likely to be set up. This is probably a factor in the grooving of angles so frequently found in boilers. Again, commercial metals and alloys almost invariably consist of mixtures, more or less intimate, of two or more constituents of different potential,

and thus are liable to set up numbers of minute galvanic That this is a fact can be readily demonstrated by placing a piece of steel in a solution of common salt containing a few drops of solution of phenolphthalein and of potassium ferrocyanide. Small points of colour soon appear, some blue and some red. The blue points prove that iron is entering into solution, while the red indicate the liberation of hydroxyl ions. Such a result can hardly be explained except by the presence of small galvanic cells, the points where iron is dissolved representing the positive plates, the negative plates being the points where hydroxyl ions are liberated. It will be seen, therefore, that it is commercially impossible to make boilers in which differences in potential do not exist, and it becomes necessary to endeavour to find what particular constituents in waters are liable to lead to corrosion, under what conditions they may be expected to do so, and how they can best be removed, or their corrosive tendencies neutralised. The working conditions likely to intensify corrosive tendencies must also be discovered.

Every one who has anything to do with the working of steam boilers is aware that an acid, such as sulphuric acid (vitriol), or hydrochloric acid (muriatic acid), obtaining access to the water will set up corrosion. The action of such acids is rapid, and occurs under any conditions, even if the water is cold. Fortunately they are readily neutralised by any alkali, such as soda ash, or even by calcium carbonate (limestone or chalk), and the resulting products are relatively harmless so far as corrosion is concerned.

Probably the natural mineral constituent in water which is best known for its corrosive tendency is magnesium chloride. It is harmless enough in itself, but is very liable to decomposition when concentrated, or in contact

with hot plates, and under such conditions hydrochloric acid is liberated, and as this will occur in actual contact with the plates it readily attacks them.

Magnesium nitrate behaves similarly to the chloride, and is at least equally corrosive in its action.

Magnesium sulphate is frequently referred to as a non-corrosive salt. Probably it is so, or at least nearly so, if present alone, but generally a water will also contain an appreciable quantity of sodium chloride or nitrate. Under suitable boiler conditions these salts interact with the magnesium sulphate and probably in the first place magnesium chloride or nitrate is formed, which in turn is decomposed in contact with the hot plates, and thus causes corrosion. It is scarcely wise therefore to call magnesium sulphate non-corrosive, as it is apt to give a false idea of security.

Even magnesium carbonate must be looked upon with suspicion. It has been previously pointed out that it is seldom found in boiler scale, owing to the readiness with which it is converted into hydrate. Probably, at times at least, it is first converted into chloride or nitrate and thus results in wasting. Except on this assumption some cases of corrosion would be difficult to explain.

All magnesium salts are likely, therefore, to be objectionable, at any rate in waters containing appreciable proportions of chlorides or nitrates.

Any chlorides and nitrates may be considered as possible factors in corrosion, inasmuch as they cause otherwise non-corrosive magnesium salts to become corrosive, as mentioned above.

Nitrates, even in the absence of magnesium salts, appear, under suitable conditions, to have corrosive properties. This is usually most pronounced in high-pressure boilers, and the higher the pressure the more

likely they are to become active or more active. In practice their virulence is found to be largely dependent not only on the temperature but on the degree of concentration, and if magnesia is absent, or present only in very small proportion, it is possible, by keeping down the concentration sufficiently, to reduce the effect of nitrates to such an extent as to be unimportant.

Carbonate of soda has of recent years gained a reputation for being corrosive, but it is doubtful whether it can be proved to be so. Undoubtedly many waters containing bicarbonate of soda naturally, do cause wasting, but probably other constituents are responsible. It is not uncommon, for instance, for such waters to contain fair proportions of sodium chloride and magnesium carbonate, and it is far easier to understand how these can lead to corrosion than sodium carbonate. Nitrates may also be present, and the working conditions such as to render them active.

The sulphates of iron and aluminium may be considered as the most virulently corrosive salts naturally present in water. They readily dissociate, forming basic salts or hydrates, and with the liberation of acid and where present in fair proportion their corrosive action is very rapid. The water in the gauge glasses is usually seen to become reddish, partly due to the iron first dissolved from the plates and afterwards precipitated, and, in the case of sulphate of iron, its own precipitation.

As previously mentioned, sulphate of iron may obtain access to rivers from steel-works. At one time such effluents were knowingly run to waste into rivers, but nowadays this is seldom, if ever, permitted. All the same, leakages are liable to occur, and may do serious damage before being detected. In some cases the corrosive liquid may slowly ooze through the walls of a building

built by the river-side, and it may even get into the river from beneath buildings erected on old tips in steel manufacturing districts. Another serious source of both iron and aluminium pollution is the slag-heaps at collieries, which sometimes contain large quantities of pyrites, and yield such impurities to the rain water percolating through the heaps. Where any of these sources of contamination are possible, the feed water should be carefully watched, and if any pollution is detected the source should be carefully looked for, and steps taken to prevent the pollution. If it cannot be arrested, a fresh feed water should be obtained if at all possible, or, failing this, carefully controlled treatment at once adopted.

Corrosion due to sulphate of alumina may also be found where oil is removed from the feed water by means of aluminoferric (commercial sulphate of alumina). In such plants it is most important that the alumina should be very efficiently removed in the treatment.

We now come to the ammonium sulphate or other ammonium salts found in the various effluents from gasplants, etc. The effects of these are similar to those of the iron and aluminium salts, ammonium sulphate decomposing in boilers with the liberation of sulphuric The danger of ammonium salts is frequently unknown, or too little appreciated. Probably some confusion arises by considering ammonium salts as ammonia itself, which is well known to neutralise acids. If an effluent containing sulphate of iron or alumina had to pass through earth before entering a water supply, it is very likely the injurious salts might be thereby more or less removed, but this would not be the case with ammonium salts, and there is thus great danger, in the vicinity of gas-works, of harmful effluents obtaining access to feed-water supplies. Among the cases of corrosion by sulphate of ammonia which have been investigated by the author, one or two may be mentioned. In one case drainage from a concreted coke-quenching bench contained ammonium salts, and found its way through cracks in the concrete to the soil beneath, percolating perhaps forty yards through the earth to a feed-water storage pond, and resulted in very serious corrosion to a large battery of boilers. In another case water used for the washing of old sacks was run to waste through a culvert originally used for blowing off boilers, the culvert discharging into a stream utilised for boiler feeding purposes. Some of the sacks had previously contained sulphate of ammonia, and the effect on the boilers fed from the stream very soon caused alarm.

It is not even necessary that the feed water should be polluted. One case, suggestive of ammonium sulphate pollution, was of a gas-works boiler fed by injector with town's water. It seemed impossible that any contamination could occur, but it was found that dust on the top of the flues of the boilers, and on the overhead beams, contained large quantities of ammonium salts, and some of this dust obtained access to the boilers when opened up for cleaning purposes, and led to corrosion.

In addition to the mineral constituents in water, the dissolved gases must be considered, as all boiler feed waters, unless previously treated, contain more or less oxygen and carbonic acid dissolved from the atmosphere. There are differences of opinion as to whether oxygen is corrosive in the absence of carbonic acid, but all agree that in the presence of even traces of moisture and carbonic acid, oxygen will readily attack iron and steel.

The corrosion due to dissolved gases in feed water is most noticeable when it takes the form of more or less

circular pittings. This is likely to occur on surfaces where there is sluggish or no circulation of the water, especially if the parts are more or less horizontal; or where, for any other reason, gas bubbles may separate from the water and remain on the metal for an appreciable time undisturbed. A particular spot having once been attacked is roughened and thereby rendered more liable to form a lodgment for further gas bubbles, and eventually the part may be pitted completely through while the surrounding metal is unaffected. Any pocket in a steam plant, where air expelled from the water may collect, is liable to be corroded, though in such cases the action is more or less general instead of in the small circular spots above referred to.

As carbonic acid is liberated when bicarbonates are heated, corrosion similar to that due to dissolved gases may sometimes be experienced from the use of waters containing temporary hardness or sodium bicarbonate, unless suitable treatment be adopted.

Probably dissolved gases play some part in the general corrosion of boilers, but it is almost impossible to speak with any assurance on this point, as this corrosion cannot be distinguished from that due to other causes.

In connection with dissolved gases we must also consider the acid gases (other than carbonic acid) present in the atmosphere of towns, and particularly in manufacturing districts. Where feed water containing little alkalinity is exposed to air in open tanks, it is always possible for acid gases to be taken up to such an extent as to neutralise the alkalinity and render the water acid. Rain water is specially liable to this form of contamination, and in manufacturing districts it is seldom wise to use rain water for boiler feeding purposes without either chemical treatment or the admixture of other water containing

Memporary hardness, which will neutralise acids dissolved from the atmosphere.

Corrosion in boilers may occasionally result from the use of greasy feed water. If pure mineral oil is used in the engines no corrosion can result therefrom, but some oils contain an admixture of animal or vegetable oil (known by the general name of fixed oils). Fixed oils are compounds of fatty acids with glycerine, and under suitable conditions they are decomposed in the boilers with the liberation of the fatty acids. Though not nearly so corrosive as the mineral acids, fatty acids certainly have the power of attacking iron and steel, and fixed oils should therefore be excluded from boilers for this reason; in addition there is the possibility of any oils causing overheating.

While considering the causes of corrosion it will be well to draw attention to the possibility of corrosive constituents obtaining access to feed supplies from agricultural land. This form of pollution is likely to be more common nowadays owing to the extensive use of artificial manures containing nitrates or ammonium sulphate, and sometimes sulphate of iron, and to the greater area of land now being put under cultivation. Water supplies, hitherto used for boiler feeding purposes for years without ill effects, may suddenly be found to cause active corrosion. Unfortunately it is often difficult to convince boiler users that a supply which has given satisfaction for years can be held responsible for corrosion, and they are more ready to blame the material of the boiler plates, especially if a new boiler has recently been installed.

Calcium carbonate, having the power of neutralising acids, has a tendency to reduce the corrosive activity of other salts, and if present in fair quantity may even completely prevent corrosion from small quantities of the harmful salts. This must be carefully remembered when water is subjected to softening treatment. Imperfect softening may result in largely removing calcium carbonate while leaving the corrosive salts, which are thus rendered more active. This has frequently been found to occur in practice, and often the softening plant has been unfairly blamed.

From a consideration of the foregoing remarks it will be seen that in order to neutralise, as far as possible, the corrosive tendency of a water, mineral acid, if present, should be neutralised; and magnesium, iron, aluminium, and both free and half-combined carbonic acid removed as efficiently as possible. All this can be done by softening treatment with lime and soda ash, except that perhaps half a grain of magnesia per gallon may be left in solution. It is also wise, where otherwise permissible, to use a small excess of chemicals in the treatment, so that the water will have a slight caustic alkalinity which will enable it to combine with any carbonic acid which may be taken up by the water from the atmosphere between the softening plant and the boiler. The same chemical treatment will also decompose ammonium salts, if present, with the liberation of free ammonia, which will not be harmful in the boilers.

Softening treatment should also effect the removal of traces of oil, thus avoiding the liberation of fatty acids in the boilers.

Unfortunately nitrates will still remain in the water after treatment, but even these will be rendered less active if magnesia has been reduced to the lowest limit; and if an excess of chemicals be used they will also have a beneficial effect in retarding the corrosive action of nitrates. By keeping boilers cleaner, and thus avoiding unnecessarily high temperature of the plates, softening treatment will

materially reduce the liability of nitrates to be decomposed, and will in this way tend to retard corrosion.

In addition to treatment, great care must be taken to avoid undue accumulation of nitrates in high-pressure boilers. It is not possible to lay down any hard and fast rules for their maximum permissible concentration, as so much depends on conditions such as the working pressure and the temperature of the plates. Where boilers are clean and lightly fired, nitrates will be much less liable to cause trouble than in dirty, heavily fired boilers.

CHAPTER IV

SOFTENING

It is not so many years ago that steam users were in the habit of putting such things as a dead pig or a sack of potatoes into their boilers as a means of preventing the formation of hard scale, but though the practice may have been permissible then, it can scarcely be recommended in these days of higher pressures and harder firing conditions. Probably any one trying the experiment in a modern boiler would pay dearly for his experience.

Nowadays it is not only necessary to exercise care in selecting the best feed water available, but to take steps to treat it in such a way as to render it as suitable as possible for the required purpose. The treatment will naturally depend on various circumstances, such as:—

- (1) The character of the water.
- (2) The type of boiler.
- (3) The rate of firing.
- (4) The length of time it is necessary the boilers should work between cleaning times.

The most common practice at the present time, where scale is formed or corrosion occurs in boilers, is to introduce some chemical or boiler composition directly into the boilers, or into the feed water before it enters the boilers. In either case the chemical reactions take place mainly in the boilers. Though this, as a rule, cannot be con-

sidered the best practice, in most cases it is better than no treatment at all, especially as regards the prevention of corrosion.

One thing should be strictly avoided—namely, the indiscriminate use of the quack remedies known as boiler compositions. Some of these consist of suitable chemicals for the treatment of certain waters, but are only satisfactory for those particular waters, and then only if used in the correct proportion as ascertained by analysis, and introduced in the right manner. Unfortunately, too many are not only useless but do harm by increasing the amount of deposit formed in boilers, while others are even liable to cause corrosion. A very few are specially prepared by the makers to suit the particular water, a sample of which they have analysed, and instructions are given as to the quantity required, and how it should be introduced. To this class no exception can be taken except on the score of price. The makers must necessarily cover themselves for the cost of the analysis by including for it in the price charged for the composition, and the analysis has therefore to be paid for time after time so long as the composition is purchased.

By far the better plan for steam users needing a boiler composition is to submit a sample for full mineral analysis to a chemist who has a thorough knowledge of this branch of his profession, who can advise generally as to the suitability of the water for use with or without treatment, state the nature and amount of chemicals, if any, required for the treatment, and whether softening is desirable or essential.

For the guidance of those who have already had an analysis made of the water to be used, but have not the knowledge necessary to interpret the results, it may be stated that in most cases either soda ash, caustic soda,

or a mixture of the two will be all that is required, though occasionally the addition of a little tannin may be useful, especially where graphitic corrosion of economiser pipes is taking place. A method of arriving at the correct mixture and deciding the quantity required will be found on page 75, but for the present it will be sufficient to state that the carbonates require neither form of soda; the sulphate, chloride, and nitrate of calcium need soda ash; while the corresponding salts of magnesium should have caustic soda. As the carbonates present will convert some of the caustic soda into carbonate, a quantity of the soda ash equivalent to the carbonates should be replaced by caustic soda. This in some cases will mean that no soda ash will be needed, and in that case caustic soda equivalent to the permanent hardness is all that is necessary.

Whatever the particular chemical introduced, it is important, if the best results are to be obtained, that it should be introduced continuously, and pro rata with the feed, so that every portion of the water receives its quota of chemical before entering the boiler. Probably the best method of attaining this is to have a small pump specially for the solution, and to have it driven from the feed pump, so that every stroke of the feed pump results in the delivery of a definite quantity of solution, and it should be so arranged that the chemical and water mix before entering the boiler.

An alternative method of introducing the chemical solution is to have a small branch pipe, with a regulating cock, on the suction pipe of the feed pump. This pipe is immersed into the solution, and the cock so adjusted that for every stroke of the feed pump the correct quantity of chemical is drawn in for the treatment of the quantity of water delivered.

A less accurate method, but one frequently sufficiently good for the purpose, is to make a solution of the quantity of chemical necessary for an average day's supply of feed water, and allow it to run, from a small tank provided with a regulating cock, into the feed tank, at such a rate as to be used up in the course of the day. If the solution tank be fixed fairly high, and the regulating cock sufficiently low, the difference in head during the day will not be enough to affect materially the rate of flow. This method is only really good when the boilers are being fed more or less steadily throughout the day, and the daily evaporation is fairly uniform.

Though a boiler of the Lancashire type may possibly work fairly satisfactorily with a water having twenty degrees of hardness, provided chemical treatment be adopted to cause the scale-forming constituents to be deposited in a readily removable form, and to neutralise those salts liable to lead to corrosion, it will usually be an advantage to put down a water-softening plant where the water has anything over ten degrees of hardness, and it is very unwise to allow water of even ten degrees to enter boilers of the water-tube type, more especially those in which small diameter tubes are used, the walls of which, being thin, allow little margin for wasting.

Where the character of the water, type of boiler, and working conditions make it undesirable that the water should enter the boilers without first removing as much of the scale-forming matter as possible, it becomes necessary to treat the water in one of the softening plants, and these may be divided into three main classes, viz:—

- (1) Exhaust Heater-Softening Plants.
- (2) Lime and Soda Plants.
- (3) The Permutit Plant.

It is scarcely necessary to enter into details of the various softening plants on the market, as full particulars of any can be obtained from the makers, but the leading principles will be briefly mentioned.

With one exception, all the types of softening plants used in this country are continuous in their action. exception is that invented by Archbutt and Deeley, which consists of a large tank (or more than one) which is filled with a definite quantity of the crude water. The requisite quantity of lime and soda ash for the treatment is then dissolved in water in a small tank, a steam jet being used to hasten the solution, and run into the large tank of crude water. The whole is then agitated for a certain time (perhaps ten minutes) depending on the character of the water, by means of air which is blown in through pipes fixed near the bottom of the tank and perforated on their under side. The air is supplied by means of a steam injector. After the agitation has been continued sufficiently long, the water is allowed to stand until the precipitate has settled out, and the clear soft water is then drawn off from the surface through a floating pipe. The mud is allowed to collect in the bottom of the tank, as, when agitated with a fresh supply of water and chemicals, it hastens the chemical reactions and the rate of settlement of the precipitate.

If a continuous supply of water is required, two or more tanks are used, so that one or more are being filled, treated, or are settling, while one is being emptied.

This type of softener is a very good one, especially if the crude water is of variable composition, as each tankful of treated water may be tested before being run off, and further chemicals added if necessary, or adjustments of the reagents made for the next tank. It has not found very much favour, however, owing to the fact that it requires much more attention than continuous plants; in fact, for a plant of large capacity one or more men may be required in constant attendance.

In the continuous plants the chemical reagents, either separately or mixed, are automatically introduced in the correct proportions by means of apparatus controlled by the incoming water. The mixture of water and reagents then enters a reaction chamber in such a way as to keep the whole in a state of more or less agitation, mechanical means for better agitation being sometimes provided. After leaving the reaction chamber, the treated water passes somewhat slowly, and without agitation, through a settling compartment, where a portion of the precipitate is deposited, and then passes through a filter or filters, usually of carefully packed wood fibre. Quartz sand filters are sometimes provided, either alone or following wood-fibre filters.

Exhaust Heater-Softening Plants.—In this type the crude water enters a chamber in which it is brought into intimate contact with exhaust steam (or live steam if desired), by which the temperature of the water should be raised to boiling-point. If the heating chamber is well designed, and of sufficient size, most of the half-combined carbonic acid will be expelled from the bicarbonates, and result in the precipitation of the calcium carbonate with the exception of a few grains per gallon, and possibly some of the magnesium carbonate may also be thrown down.

If a water contains permanent hardness, a solution of soda ash is introduced uniformly into the water, either before it enters the heater, or immediately after leaving it. By this treatment the salts constituting the permanent hardness are converted into carbonates, and will be precipitated if present in quantity exceeding their maximum solubility in boiling water.

The heater in these plants should be so designed as to expose the water in thin films or drops to the action of the steam, otherwise the half-combined carbonic acid may not be efficiently expelled, and the best results will not be attained. As a rule the water is made to run over a series of trays, sometimes perforated, and to fall in thin films or drops from one tray to another. After leaving the heater the water passes into a suitable settling chamber, where a portion of the precipitated solids may be deposited, and the partially clarified water is then filtered, usually through beds of carefully packed wood fibre. This type of plant is very useful for utilising exhaust steam which would otherwise be blown to waste, as it not only saves the valuable heat of the steam, but results in a supply of hot feed water so much appreciated by engineers. It has the advantage of simplicity of control, only one chemical being required, and that a freely soluble one which gives a true solution, easy of manipulation.

The oil present in the exhaust steam becomes entangled in the precipitate, and provided the water is hard enough to give a sufficiently large precipitate for the purpose, the oil may thus be efficiently removed. In order to render the removal of grease as perfect as possible, it is usual first to pass the steam through a mechanical oil separator, and the best plants are usually provided with such an apparatus.

Unfortunately this system does not usually result in very thorough softening unless lime is introduced as well as soda ash, owing to the solubility of magnesium carbonate, and in some cases, even though the plant be worked at its highest state of efficiency, the treated water, though much improved, may still have a fairly high degree of hardness. Again, the remaining hardness in such

cases is likely to be due mainly to magnesium carbonate, which is liable to form a light floury deposit which may lead to priming and overheating troubles unless special care be exercised in the working of the boilers.

Lime and Soda Plants.—These constitute the great majority of the softening plants used at the present time, and may well be subdivided into two classes, viz:—

- (1) Those in which the lime is introduced in the form of clear lime water.
- (2) Those where the lime is introduced in the form of milk of lime.

Few of the former type are made now, though at least one prominent maker still adheres to the principle, claiming that where magnesium is present in large proportion it can be more effectively removed by lime water than by the more concentrated milk of lime. It is doubtful whether this claim can be upheld, as very efficient softening is frequently attained with the latter form, even with waters of very high magnesia content. Probably either form of introducing lime gives equally good results, but owing to the usually greater cost of plants for the limewater process (on account of the need for a large vessel for the production of the necessary solution), the milk of lime plants find a readier market, especially as they are also more compact.

Lime-Water Plants.—Where lime water is used, a definite proportion of the crude water is by-passed to the bottom of a tall inverted conical vessel, which is regularly charged with fresh supplies of slaked lime. In the lower portion of the cone the incoming water keeps the solid particles of slaked lime in a state of agitation, and the water thus becomes charged to its saturation point with lime. As the solution rises in the cone, its rate of flow

decreases as the diameter increases, and most of the solid particles are left behind. By the time the water reaches the outlet at the top of the cone it is in the form of fairly clear, saturated lime water. The fraction of the water necessary to be passed through the saturator is usually divided from the main supply by allowing the crude water to enter a tank, known as a dividing box, which is fitted with weirs of adjustable width, so that any required proportion of the whole may be by-passed. With this type of plant soda solution has to be made and introduced separately, involving further cost of manufacture in providing the additional gear for the purpose, and to a certain extent complicating the working of the plant. Various methods are used for the introduction of soda ash in such cases, but the description of these would occupy too much space. Probably the principal types are those involving the displacement of the soda solution by a bypassed fraction of the crude water, and those in which a portion of the water is passed through a device in which it should dissolve a definite amount of soda, and leave as a solution of constant strength, no matter what quantity of water is being thus by-passed. There is always apt to be a feeling of uncertainty whether such types are working correctly, and irregularities in the working cannot be detected by observation. In some cases also trouble is experienced in the constant strength solution devices. owing to soda crystallising out and choking up the apparatus.

Milk of Lime Plants.—In this type it is usual nowadays to have both the lime and soda ash in one solution. The lime necessary for the treatment of a certain quantity of water is slaked, the requisite amount of soda ash added, and the whole diluted to a definite volume. This mixture, usually known as the *reagent*, is passed through a fine

sieve to remove coarse grit and stones, into a tank known as the reagent container.

Several methods are in common use for the apportioning of the reagent, the principal being:—

- (1) Tipping-bucket.
- (2) Lift pipe.
- (3) Displacement.

The tipping-bucket method is the most generally adopted. It is very simple, and any irregularity in working is readily noticeable. There may be either a single or a double bucket, but in either case the crude water runs into a bucket which, when full, automatically tips and empties itself. The tipping movement actuates the gear for introducing a measured quantity of reagent sufficient for the treatment of the amount of water tipped. The reagent measuring gear may consist of:—

- (a) Cups or scoops which are filled by passing through the reagent when the bucket tips, the scoopful being delivered into the tipped quantity of water.
- (b) Valves in the bottom of the reagent containers, which open when the bucket tips, and allow a certain quantity of reagent to pass. At one time these valves were frequently taper valves, which allowed the solution to flow during the time they were open, but as the quantity thus discharged varied with the head of solution in the tank, they are now more frequently made on a different principle, so as to deliver a measured quantity of reagent independent of the head.

It was found in practice that for large plants the great momentum of the tipping of a large volume of water resulted in such severe strains that the gear was apt to get out of order very quickly. Various methods have been adopted for overcoming this defect,

usually by some form of buffer. One type of buffer consists of a chamber on the under-side of the bucket. When the bucket tips, the open side of the chamber comes in contact with water in the tank in which the tipper works, and air is imprisoned and more or less compressed, thus forming a cushion. A small adjustable vent in this air chamber allows the imprisoned air to escape gradually, thus permitting the bucket to sink slowly to its lowest normal position. A more recent method of overcoming the momentum difficulty, possibly the most successful method up to the present, is to have a small tipping-bucket actuated by only a portion of the incoming water, which is divided off from the main stream of water by means of an adjustable division on a weir over which the water has to flow.

The lift-pipe gear has a pipe in the reagent tank, the lower end of the pipe being connected by a flexible joint to an outlet pipe at the bottom of the tank. The other end of the lift pipe is connected by a chain passing over a pulley to a float in a small tank known as the regulating tank. When the reagent tank is full, the regulating tank is empty, and the length of the chain is so adjusted that the top of the lift pipe is just above the level of the reagent. A small definite proportion of the incoming crude water is divided off, and allowed to flow into the regulating tank, the float being thereby gradually raised, and the lift pipe consequently lowered, thus allowing the reagent to pass through it to mix at a suitable point with the main stream of water. The quantity of water by-passed for the regulation is so adjusted that the regulating tank is full, and the reagent tank empty, by the time the quantity of crude water for which the charge of reagent is intended has entered the plant. A slight disadvantage of this type is that after a charge of reagent

has been used up, the plant has to stop for a short time while recharging.

In the displacement method, a small portion of the incoming water is divided off by means of an automatically adjusting division in a dividing box, and allowed to enter the reagent chamber and thus displace an equal quantity of reagent, which then mixes with the main stream of crude water. As the reagent is thus gradually weakened, it becomes necessary to allow an increasing proportion of the total water to enter the reagent tank. This is accomplished by an ingenious contrivance, operated by the flow of water into the plant, by means of which the adjustable division in the dividing box is automatically moved to permit an increasing proportion of water to pass, the rate of increase becoming greater as the strength of the reagent decreases. The advantage claimed for this method is that no moving parts utilised for measuring purposes come in contact with the reagent. On the other hand, the adjustable weir, and the mechanism controlling it, are somewhat more intricate and delicate than is usually considered desirable in connection with softening plants, and any irregularities would be less easy to detect and rectify than in simpler types of apparatus.

Permutit Plant.—This is a system of softening in which no chemicals whatever are added, and normal variations in the composition of the water do not affect the results of treatment, which is therefore rendered very simple.

The water to be treated is passed through a bed of an artificial mineral known as Permutit. This consists of a complex silicate of aluminium, sodium, potassium, calcium, magnesium, etc., and is an imitation of a natural mineral known as Zeolite.

When water containing hardness-forming salts comes into contact with Permutit, a chemical interchange takes place, the calcium and magnesium being taken from their salts, and sodium and potassium substituted. The hardness of the water may thus be entirely removed.

After Permutit has removed a certain amount of hardness, its power is reduced and eventually exhausted, but it is revivified by passing through it a fairly strong solution of common salt (sodium chloride), which brings about a reverse reaction, removing from the exhausted Permutit the calcium and magnesium taken up from the water, and replacing them by sodium, thus restoring the original condition, and enabling it to soften water once more.

Usually, in practice, plants are made of such size as to efficiently treat the particular water at the necessary rate for a certain number of hours, after which salt solution is passed through the plant to regenerate the Permutit. It is claimed that this can be continued indefinitely.

For waters practically free from temporary hardness, this process is a very useful one, and in any case it is so for the treatment of water for laundry purposes and processes where entire freedom from hardness is desirable. When temporary hardness is present, however, sodium bicarbonate is left by the treatment, practically equal in amount to the temporary hardness removed. As it is usually considered objectionable to allow sodium carbonate to accumulate in boilers, this must be looked upon as a distinct drawback to the process, especially as the cost of removing temporary hardness by Permutit is exactly the same as for permanent hardness, whereas by lime treatment temporary hardness can be removed, on an average, at about one-sixth the cost of permanent hardness.

It is perhaps only fair to say that the makers of the

Permutit plant maintain that the carbonate of soda produced by the process is not objectionable in boilers, provided that the internal gun-metal fittings are of good quality. It is difficult to believe that sodium carbonate thus formed can differ in its effects from that added as soda ash, or from the carbonate present naturally in certain water supplies.

CHAPTER V

SELECTION OF SOFTENING PLANTS

Whenever possible, unbiased expert advice should be obtained by those considering the purchase of a softening plant, as it is of the greatest importance that first cost should not unduly influence the choice. An efficient plant, which will continue to perform its duties for a reasonable time without repair or frequent adjustment, is a blessing to a steam user. On the other hand, an inferior article may cause endless trouble, and many plants have been discarded owing to the difficulty of obtaining satisfactory results. Imperfect softening, instead of removing the corrosive tendency of a water, sometimes increases it, while in other cases it may lead to choking up of pipes and valves.

A few words of advice based on years of experience will not be out of place.

Size.—In the first place the plant should be of ample size. This does not mean that a plant should be obtained with a rated capacity higher than is required. The chemical apportioning gear should be designed for satisfactory working at the maximum rate necessary, but no more. It is the reaction and settling chambers which need to be large, and they should always be of such size that the water will take at least two hours to pass through them, i.e., a plant for the treatment of one thousand gallons per

hour should have reaction and settling tanks with a capacity of not less than two thousand, and preferably three thousand gallons. In special cases even larger tanks are an advantage.

Strength.—All parts of the plant should be of ample strength for standing the necessary strains or pressure. This applies particularly to exhaust steam heaters, which, having to stand sudden changes of pressure and a wide variation of temperature, are liable to be distorted or even ruined unless substantially made. They should be constructed of stout materials, and be well stayed.

Reagent Gear.—Moving parts of the chemical apportioning gear should be well designed and strongly made to withstand reasonable wear and tear for long periods without undue attention, adjustment, or repair. It should be so designed as to work uniformly whether the reagent tank is full or nearly empty, and all parts liable to choking up should be visible and readily accessible for cleaning purposes. In the case of tipping-buckets, they should be so sensitive in action that they can be relied upon always to tip immediately when filled to a definite point, not being unduly influenced by rust or dirt in the bearings, or deficient lubrication. Any special arrangements for increasing the sensitiveness should receive careful consideration.

The apportioning gear should work satisfactorily, when required to do so, at much below the rated capacity. Special devices for keeping the reagent continually stirred must therefore receive consideration even though the price of the plant may be thereby increased. When the plant is working slowly the suspended particles of lime in the reagent are liable to be deposited on the bottom of the reagent tank unless constantly stirred, thus leading to want of uniformity in the strength of the reagent.

Recharging.—If inconvenience would result from the stoppage of the plant for the purpose of recharging with reagents, care should be taken to select a plant which can be recharged while working.

Reagent Capacity.—The reagent tank should be of such size as to render frequent charging, or recharging at inconvenient times, unnecessary.

Preparation of Reagent.—Convenient arrangements for the preparation of fresh supplies of reagent in readiness for recharging should be provided. These should be readily accessible, so that the man in charge has not to climb ladders, or be in awkward positions while mixing the reagent. This is particularly important in bad weather, as otherwise the plant may be neglected. If possible, suitable gear should be provided at ground level.

Accessibility.—If it can be conveniently arranged that all parts which it is desirable should be kept under observation (such as the apportioning gear) are at, or near, ground level, or in some readily accessible place, the plant will necessarily be kept under closer observation than if placed high up, or in some out-of-the-way corner. In any case safe ladders should be provided for reaching all parts requiring attention. Flat step ladders are preferable, and hand-rails should be provided.

Short-circuiting.—Reaction and settling tanks should be of such shape and dimensions that the water will not be liable to take a short cut across from the inlet to the outlet, and thus render a portion of the tank useless. If tanks are of large area this is almost sure to occur. Where a tank of large area is the most convenient, it should be divided off into two or more compartments, the water passing through them either in series or in parallel. Vertical cylindrical tanks are the best for avoiding short-

circuiting, and are to be recommended where in other respects they are equally convenient.

Direction of Flow.—To obtain the best results water should pass through the settling tanks in an upward direction in order that precipitate, which has a natural tendency to fall, may be separated from the water as quickly as possible. If the water passes downwards, not only does it follow the downward tendency of the sediment and thus reduce the rate of separation, but on leaving at the bottom of the tanks the water may tend to carry along with it some of the mud already deposited there.

Sludging.—All settling tanks should be provided with convenient and effective sludging arrangements, otherwise mud will collect to such an extent as to interfere with the speedy clarification of the water. In this connection it may be said that, though it is impossible to keep settling tanks too free from deposit, an exception must be made in those cases where one tank acts both as reaction and settling tank as in the case of the vertical cylindrical plants. When reagents and water have mixed, the chemical reactions are hastened if the water is allowed to agitate and mix with old precipitate, and larger particles of precipitate are formed which separate more quickly from the water. In such plants, therefore, it is not advisable to keep the bottom of the tank too clean, though, of course, undue accumulation of mud should be prevented by the regular use of the sludging gear.

Filter Area.—The filter or filters should be of such area that the water passes through at slow speed. As a rule wood-fibre filters are used, and if worked at too high a speed they are not effective. Even when two or more are used in series it is very desirable that *each* should be of ample area. Too much reliance must not be placed on wood-fibre filters. Though, if properly used, they are

usually satisfactory in softening plants, unless the fibre is carefully packed (especially in the corners) and cleaned sufficiently often, they are liable to allow precipitate to pass through. If they are required to do much work, frequent cleaning will be necessary, and this is usually found very inconvenient. Provided the settling capacity is great enough, little work is left for the filters, and they may work for months at a time.

Water should always pass through wood-fibre filters in an upward direction.

Sand Filters.—In cases where the most efficient filtration is needed, a sand filter following the wood fibre is an advantage. This may sometimes be necessary where perfect elimination of oil is required, and where the plant does not provide sufficient time for the sedimentation. The oil being entangled in the precipitate, it is important that this should be efficiently removed.

Sand filters, when dirty, instead of passing imperfectly filtered water, choke up, and so demand the attention which they might not otherwise receive.

Storage.—In almost all cases a softened water storage tank is desirable, in order that a supply of treated water may be available in case of a hitch in the working of the plant necessitating temporary stoppage. The size of the storage tank must depend on the working conditions in each particular case, but frequently a storage sufficient to supply small requirements during the night is put down, so that the plant need only be worked during the day.

Painting and Housing.—All external parts of the plant should be well painted to protect them from rusting, and it is always an advantage if the whole plant can be erected indoors. Failing this, housing the working parts is desirable, and usually results in the plant being kept cleaner and receiving closer attention.

CHAPTER VI

PRIMING

UNDER certain conditions, water is carried over with the steam from boilers. This is due to the steam bubbles, instead of bursting on the surface of the water, rising unbroken into the steam space and more or less filling it, some being carried right into the steam pipes. This is generally known as *priming* or *foaming*.

Priming may well be subdivided into two classes: "Foaming" and "Bumping."

Foaming may be considered to be the partial or complete filling of the steam space with a froth somewhat resembling soap lather, composed of numerous comparatively small bubbles of steam. In other words, it is too free ebullition. This may occur when:—

- (a) The nature of the water is such as to form a froth when violently agitated. Soap or certain other organic matter such as Irish Moss may do this.
- (b) There is too free a liberation of steam bubbles due to small particles of matter, suspended in the water, acting as nuclei for the formation of steam bubbles. Up to a certain point these suspended particles may be useful in causing smooth ebullition, but when present in excessive

quantities, small bubbles of steam may be liberated so freely, and in such large numbers, as to produce a foam somewhat similar to that due to soap.

Bumping.—This term may be used to imply intermittent or explosive boiling, or, in other words, retarded ebullition. If the condition of the water is such as to interfere with the free formation or liberation of steam bubbles, the water may be quiescent for a short time and become superheated, and then large steam bubbles are likely to be formed suddenly and rise to the surface, where they may burst with sufficient violence to throw some of the water into the steam space, and possibly into the pipes. This may occur:—

- (a) With certain solutions, such as caustic soda, which have a great tendency to boil intermittently in this manner.
- (b) If a film forms on the surface of the water, thereby preventing the free liberation of steam. This is particularly noticeable in laboratory work when a highly saline solution is being evaporated. A point is reached when a very thin crystalline film is formed on the surface of the liquid, preventing or retarding evaporation. The liquid then becomes superheated until the vapour pressure is sufficient to burst through the skin, when the steam will be liberated with violence. A film of oil on the surface may cause a similar result.

Probably one of the most frequent causes of priming is the presence in the water of light particles of solid matter in suspension. It is a regular practice in laboratories, when a liquid is liable to boil explosively, to in-

troduce small pieces of pumice, platinum wire, capillary glass tube, or a very small quantity of zinc dust. Such things act as nuclei for the formation of the steam bubbles, which then form freely and continuously, and the liquid boils quietly. Whatever is used for the purpose, it is important that it be introduced carefully, otherwise, at the moment of introduction, the liquid is very likely to froth up, and possibly overflow the containing vessel. In the case of zinc dust this effect is most pronounced, and if much be added the foaming will continue to an undesirable extent.

We will now consider how the foregoing remarks apply in the case of boilers. Finely divided suspended matter is likely to act similarly to zinc dust, the finer the particles, and the greater their number, the greater will be the foaming effect. Some particles will have only a useful effect in assisting free ebullition, while others may cause it to be excessive and lead to priming. Magnesium salts, when precipitated in a boiler, are apt to form a light floury deposit, which is probably the most likely substance to act in this way. Up to a certain extent this may be beneficial, but in excess it will very probably lead to undue foaming. The light floury magnesia precipitate is usually formed when magnesium salts predominate, and may therefore be present where imperfect softening has resulted in the removal of most of the calcium salts while leaving the magnesia.

Again, as already stated, at the moment of introduction of substances which act as nuclei, sudden foaming usually results. Such a condition may readily occur in boilers under certain circumstances. If a water be irregularly treated, either in a softening plant or by the admixture of chemicals without a softener, the water in a boiler may contain either permanent hardness or an excess of the

chemical used. If the water in a boiler contains permanent hardness and an excess of soda enters, or vice versa, a sudden precipitation occurs which may act similarly to the introduction of zinc dust, and have much the same result—namely, excessive foaming. This probably has a bearing on the much-discussed question as to whether excess of sodium carbonate causes priming.

There is no doubt that boilers containing an excess of sodium carbonate do frequently prime, yet there must be many boilers with at least an equal excess which do not. Moreover those which prime do not usually do so continuously, as might be expected were the soda to blame. Probably, in such cases, the trouble is due to permanent hardness entering the boilers and resulting in the sudden formation of a precipitate. This may readily be demonstrated by boiling a solution of sodium carbonate, and then adding a solution of any salt (such as magnesium sulphate) which will form a precipitate. Immediate foaming will result.

A similar effect may be obtained by introducing a small piece of hard scale, say a calcium sulphate scale, into a boiling soda solution. In this case the disintegration of the scale produces the fine particles necessary to cause foaming. This may often occur in boilers where there is old scale on the plates, and where an excess of soda is used in the treatment of the feed water, pieces of scale becoming detached and disintegrated.

It is a common complaint, when softening plants are installed, that the softened water causes priming. It may certainly lead to priming by loosening old scale, but had the boilers been thoroughly cleaned before commencing treatment there would probably have been no trouble. It may be argued that this explanation is incorrect as many boilers are thus fed without ill-effect although they

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contain scale, but it must be remembered that moderate foaming is rather beneficial than otherwise, and may therefore occur in many cases unnoticed, while in others, owing to the different character of the scale, the greater excess of soda, or other circumstances, excessive foaming may result.

Mineral precipitates in a boiler are not the only finely divided substances liable to cause foaming. Organic matters in suspension are quite likely to lead to such results if present in sufficient quantity, especially those of a more or less colloidal nature.

Soap occasionally obtains access to feed-water supplies and causes foaming, while in other cases it may actually be formed in boilers by the saponification of fixed oils by soda.

Bumping probably occurs less frequently in boiler practice. The concentration of caustic soda necessary to lead to bumping is not usually reached, and only very excessive concentration of salts would lead to the formation of crystalline skin on the surface of the water, but it is quite possible for either condition to be present. An oily scum is more likely to be present, but even this is not common nowadays, most steam users avoiding the introduction of oil in such quantities as would bring about such a result.

A slight tendency to foaming may be intensified by the working conditions and become objectionable priming. Such aggravation may result from sudden excessive demands on the steam, as in the case of winding engines at collieries, and other engines which work intermittently; also where steam is used for boiling water as in the case of laundries. If a number of washing machines require steam at the same time, the supply may not be equal to the demand. In all such cases, excessive demand results in a

sudden reduction of the steam pressure in the boilers, and the boiling-point of the water being thus lowered, the water becomes superheated, and will boil vigorously until the balance is restored. If the tendency is already there, priming is likely to result. It is most important, where sudden demands on the steam are unavoidable, that boilers with large steam spaces be used, or, as an alternative, steam reservoirs installed.

Having discussed the most likely causes of priming, it will be well to mention the best methods of avoiding it.

- (1) Ample steam space should be provided, especially where sudden demands are unavoidable.
- (2) Soapy water should be carefully excluded, and also oil, especially if it contains fixed oil which may saponify and thus form soap.
- (3) Excessive accumulation of any saline matter, especially caustic soda, should be avoided by the regular use of the blow-off cock, and sufficiently frequent emptying of the boiler.
- (4) Prevention, if necessary, of undue accumulation of fine particles in boilers:—
 - (a) by avoiding suspended matter in the feed water, filtering if necessary;
 - (b) by adopting efficient softening if the water is hard, taking special care to reduce magnesia to the lowest possible limit;
 - (c) by, in any case, removing as far as possible (by the regular use of the blow-off cock) such deposit as cannot be avoided. It may be well here to draw attention to the effect of opening the blow-off cock of a boiler. While working, a more or less uniform layer of deposit will probably be formed on the bottom of boilers. When the

blow-off cock is opened, the deposit over it, and in the immediate vicinity, first runs out, but afterwards water containing only a comparatively small proportion of sediment leaves, and the remainder of the deposit on the bottom stays behind. After closing the cock the deposit gradually levels itself again over the blow-off pipe, so that after a time a further quantity may be removed as before. Opening the blow-off cock several times for a few seconds has therefore a much greater effect in removing deposit than blowing off the same amount of water in one operation. It must not be overlooked. however, that frequent opening and closing of the cock leads to wear and tear, and it is for the engineer in charge to decide how often it is necessary in any particular case.

(d) Whatever treatment, if any, be adopted, should be as uniform as possible, in order that permanent hardness and soda entering the boiler alternately may be prevented.

In connection with priming it must be borne in mind that it may be not only a source of danger by water-logging the steam pipes, and thus allowing water to enter the engine cylinders, but it is conceivable that priming in the tubes of a water-tube boiler, especially where the tubes are of small diameter, might lead to the temporary partial emptying of one or more tubes, and consequent overheating.

CHAPTER VII

SCALE, GREASE, AND OVERHEATING

SCALE in boilers is so common that all who have anything to do with steam boilers are well acquainted with it, and very little need be said on the subject.

In most cases it is very difficult to offer a definite opinion as to the character of the scale likely to be formed from any particular water, as so much depends on working conditions. Where the hardness of a water consists almost entirely of calcium sulphate it is fairly safe to predict that the resulting scale will be of a hard nature whatever the conditions, but beyond this it is seldom safe to venture. Magnesium salts have a tendency to form a light floury deposit, but in combination with other constituents may produce a very hard scale. In any case the character of a scale may change after it is first deposited, owing to the temperature of the plates, and mud or soft deposit in boilers is frequently baked, and thus hardened, when boilers are emptied while hot.

There is no doubt that scale or deposit of any character will have some effect in retarding the passage of heat through the plates of a boiler, and it is often contended that it results in serious loss of heat. This is open to doubt, however, as, except in exceptional cases, the imparting of heat to the water may be only transferred from one part of the boiler to another, and the temperature of

the gases entering the chimney will not be materially different in a moderately scaly boiler from that in a fairly clean one. Where economisers are used it may be said that probably little loss of heat results from moderate scale in the boilers.

It must not be thought that if there is no loss of heat scale is unobjectionable. In the first place, the expense of scaling boilers is often a very serious item in the working costs. Again, it may be decidedly inconvenient to shut down boilers for the time necessary for proper scaling, and it is not uncommon for boilers to be allowed to get into a serious condition owing to the impossibility of temporarily dispensing with their services.

Another drawback to scale is the fact, referred to previously, that it sometimes assists corrosive constituents to be more virulent. Many very serious cases of corrosion occurring beneath scale may be found in boiler practice, and such wasting sometimes goes on unnoticed until a plate has become dangerously thinned, if not actually perforated.

A further and very important ill-effect of scale is the increase in the temperature of the plates (overheating) which will result to a greater or less extent, dependent on the character and amount of the scale, the parts of the boiler on which it is deposited, and the rate of firing of the boiler. As a rule, in the absence of grease in the scale, the degree of overheating will not be such as to lead to definite evidence at the part or parts where it occurs, but may result in generally increased strains, and thereby possible leakages at seams.

Overheating becomes very much more pronounced when oil is present in the scale or deposit. In such cases local effects are very likely to be found, such as bulging or ovality of furnace tubes, bulging of shell bottoms, and bulging or hogging of the tubes in water-tube boilers.

It is surprising how little grease in scale may lead to distortion where the rate of firing is high, or where for some reason the flames impinge on one particular part. As little as one-tenth per cent. of grease in scale or deposit may cause such results, whereas boilers fired more easily may work for years without trouble with a much greater proportion of grease.

An idea exists among many steam users that if the water is soft a small quantity of grease is of little moment. This is incorrect, as, with a certain proportion of oil in a water, the lower the amount of scale-forming matter the higher will be the percentage of grease in the deposit formed, and therefore the greater the risk of overheating troubles.

Grease cannot be totally removed from steam by mechanical means such as adopted in the various types of oil separators. These usually consist of devices for causing the steam to impinge on baffles and thus changing its direction, or suddenly reducing its pressure. Undoubtedly such methods will effect the removal of a good deal of oil, but the more volatile portions of the oil will be in the form of vapour and will remain as such in the steam until it is condensed.

On the other hand, grease cannot be efficiently removed from water by simple filtration through cloths, coke, wood-fibre, or such-like.

Where overheating troubles due to oil are experienced, it becomes necessary to eliminate it totally from the water, or at least to reduce it to a negligible amount. This may be accomplished by what is known as coagulation. A precipitate is produced in the greasy water, and the tiny globules of oil are thus enclosed in, or entangled by, the

precipitate. The precipitate is afterwards removed by sedimentation and filtration.

The coagulation process is usually carried out either by softening treatment or in a plant similar to a softening plant. If the water contains sufficient hardness (the amount necessary for the purpose depending on the proportion of oil), ordinary softening should efficiently entangle the oil, and, provided the precipitate be completely removed, the water should be suitable for use in boilers. The precipitate formed by magnesium salts is more effective for grease removal than that from calcium salts.

Where the water has not enough hardness to give a sufficiently large precipitate, it becomes necessary to introduce another coagulent, aluminoferric (commercial sulphate of alumina) being usually chosen. To some extent aluminoferric may be precipitated by the temporary hardness (if any) in the water, but usually a precipitant has also to be used, caustic soda being the best for the purpose. Care must be taken that the aluminoferric is completely removed, otherwise corrosion may result. The aluminium hydrate precipitate formed in these cases is of a gelatinous nature and is a very effective coagulent, much better than either lime or magnesia precipitates.

In plants using aluminoferric, it is important that it be introduced and distributed throughout the water before the precipitant (caustic soda) is added, otherwise the precipitate may all be formed in a comparatively small area, and the globules of oil in the remaining water may escape entanglement.

An electrical process is on the market for de-greasing water, and is useful where the necessary electric current is to be obtained sufficiently cheaply, as in the case of electric generating stations. It is known as the DavisPerrit process, and consists of passing the water between two steel or iron plates fixed parallel with one another and fairly close together. An electric current is passed between the plates through the water, iron being thereby dissolved from the anode and precipitated in the water, entangling the oil The precipitate is afterwards removed by filtration.

By efficient de-greasing treatment it is usually possible to remove oil to such an extent that not more than 0.02 grain per gallon remains.

It is usual in cases where water from condensing plants is used for boiler feeding purposes that grease eliminating plants become necessary. Whenever possible, in such cases, whatever type of condenser be used, the steam should be passed through an efficient oil separator before being condensed, as the greater part of the oil is thereby removed, thus increasing the efficiency of the degreasing process.

In the case of surface condenser waters required for boiler feeding purposes, it is almost always necessary to have some make-up water, and frequently the make-up is of such a character as to render softening desirable. Where this is so, the proportion of condensate to make-up usually varies more or less considerably, and the mixture is difficult to treat uniformly. The best plan is to have separate plants—one for softening the make-up, the other for degreasing the condensed water. In most cases this is considered to be too expensive, or to require too much supervision.

An alternative plan is to have only one plant, but the reagent gear must be operated by the make-up water only, the condensate and make-up mixing when the latter has left the tipping-bucket or other measuring device. The reagents introduced will-need to be those required for the

treatment of the hard water, plus aluminoferric and a suitable proportion of precipitant. It is essential for the success of this method that the supply of make-up water shall be continuous, otherwise some condensate will pass through the plant untreated. The condensate should also be supplied as uniformly as possible.

As the hardness of the water cannot be reduced below a certain degree, no matter how low it is originally, it follows that the plan of having separate plants will result in a much less sedimentary feed supply. Supposing the hardness can be reduced to two degrees, and that ten per cent. of the total water consists of make-up, then with separate plants there will be ten per cent. of water with two degrees of hardness, and 90 per cent. with none, or one-fifth of a degree in the mixed supply. If one plant is used the whole supply will only be reduced to two degrees.

CHAPTER VIII

METHODS OF ANALYSIS

For the convenience of chemists engaged in other branches of the profession who may be called upon to make an occasional analysis, a description of the methods used by the author for a number of years, and proved to be thoroughly satisfactory, will probably be useful. In order to make them as helpful as possible they are given in some detail, and the size of apparatus found most convenient is given. Hints are also included as to the best order of commencing the various determinations. The quantities of water used are in some cases less than those recommended by many chemists, but are sufficient for all practical purposes, except in special cases, when larger quantities may be used at the discretion of the analyst.

Many attempts have been made to devise quicker methods, but the results obtained by them are not usually sufficiently accurate or reliable, and as a rule, little, if any, time is saved. A complete analysis of a sample of water can be comfortably carried through in an eight-hour day, with some spare time between operations. Where a number of samples are to be analysed they are most conveniently done in batches of four, which can be completed in two days.

The strengths of the reagents will be given in another chapter.

In order to avoid delay, the following order for starting the various estimations may be found useful when commencing analyses. The determinations of dissolved gases, Carbonic Acid and Oxygen, should first be commenced if these are required. If an estimation of Suspended Matter is desirable, the sample should then be well shaken and a portion measured off for the purpose, the remainder, or as much as necessary, being filtered for the other determina-Should it be unnecessary to estimate the Suspended Matter, it may be possible to decant the clear water without disturbing the sediment. Next measure out the quantities for Lime and Sulphates and commence the evaporations after acidifying. When these have been started, commence the Total Solids and Chlorine quantities of the first sample, and determine its Alkalinity. The pipette can then be rinsed with the second sample, and the same determinations put in hand, the other samples being thus started in turn. Nitrates should not be commenced till the Chlorine determinations have shown how much water is to be used. Ammonia may be estimated at any convenient opportunity.

Free Carbonic Acid should be estimated as soon as the bottle is first opened. If suspended matter is present it should be allowed to subside before opening the bottle, so that the quantity for this estimation may be decanted rather than filtered.

Decant 100 c.c. into a stoppered 100 c.c. cylinder, and compare against 100 c.c. of well-boiled and cooled distilled water in a similar cylinder. Add ten drops of phenolphthalein solution to the blank, and then Standard Sodium Carbonate solution from a 10 c.c. burette, one drop at a time, stoppering and gently mixing between each addition. When a faint permanent pink colour is obtained, note the burette reading. Test the sample

similarly, but with this the standard solution can usually be introduced, several drops at a time to begin with. Continue till a permanent tint is obtained about equal to that in the blank.

The number of c.c. of Standard Sodium Carbonate required by the sample, less that needed by the blank = grains of Free CO₂ per gallon.

Suspended Matter need not as a rule be estimated, as it will usually vary so widely in samples from the same source, but if required 1000 c.c. (less if much present) of the thoroughly shaken water is filtered through a 12½ cm. folded filter which has been washed with water, dried, and weighed. Wash, dry, and weigh again.

Weight of Suspended Matter in grammes from 1000 c.c. of water \times 70 = grains per gallon.

Lime, Magnesia, and Silica.—Evaporate 250 c.c. to dryness with about 5 c.c. of hydrochloric acid in a 6 in. porcelain dish, finishing the evaporation on a steam hole. Cover with a clock glass and gently heat over a small flame till any organic matter is thoroughly charred. When cool, add 5 c.c. hydrochloric acid and 5 c.c. water, cover, and simmer gently for about two minutes. Filter through a $5\frac{1}{2}$ cm. ashless paper ($1\frac{1}{2}$ in. funnel) into a tall beaker (3 in. $\times 1\frac{1}{2}$ in.), rubbing the last traces of silicious matter from the dish with a clean finger.* Wash the filter paper and silica three times with hot water. The filtrate, which should usually be about 30 to 35 c.c. and contains the lime and magnesia, together with iron, alumina,

* Occasionally when much calcium sulphate is present it may not be dissolved completely in the 10 c.c. of the diluted acid. In such cases it is readily noticeable, being a heavy, white powder, easily distinguished from the almost invisible gelatinous silica. When this is found, the solution should be decanted through the filter and a little more water and a drop or two more acid used to complete the solution of the calcium sulphate.

and manganese if present, may then be removed. Complete the washing of the filter, and ignite and weigh the silica.

Weight of Silica in grammes \times 280 = grains per gallon. To the filtrate from the silica add two or three drops of bromine water (more if much manganese is expected) and then ammonia (.95) till the colour of the bromine is destroyed and there is a slight smell of ammonia. About 5 c.c. of ammonia will be required, and only about two drops excess should be used. Cover the beaker with a watch glass, and heat in a steam hole for two or three minutes. If any precipitate forms, the beaker must be allowed to remain in the steam hole till the precipitate has satisfactorily coagulated, after which it is filtered through a 7 cm. ashless filter (11 in. funnel) and the precipitate dealt with for Iron, etc., as described later. Transfer the beaker of hot solution (or filtrate if there has been a precipitate) to the top of the bath, add 3 c.c. of ammonium oxalate solution drop by drop, while shaking or stirring with a glass rod (if stirred, the rod should not be allowed to touch the sides or bottom of the beaker). Stir or shake occasionally till the precipitate settles fairly quickly, and if much lime is present add a few more drops of ammonium oxalate to test if precipitation is complete. Keep the beaker on the bath for not less than half an hour, and not more than one hour, by which time the precipitate should settle quickly after shaking, and leave the supernatent liquid clear. Filter through a 7 cm. ashless paper, collecting the filtrate in a tall beaker $(4 \text{ in.} \times 1\frac{3}{4} \text{ in.})$. Wash six times with small quantities of hot water, retaining only the first three washings. Ignite the precipitate and weigh as CaO. The final ignition may be for three minutes over a blowpipe, or five minutes over a No. 4 Meker burner if a platinum crucible is used. Longer

ignition is necessary for specially large precipitates. In order to make sure that the lime is properly calcined, it should be tested, after being weighed, by slaking it with a few drops of water, and then adding hydrochloric acid.

Weight in grammes \times 280 = grains of CaO per gallon. Cool the filtrate from the calcium oxalate, and transfer it to a conical flask (150 c.c. Registered Pattern). Add slowly, while shaking the flask, 3 c.c. of a saturated solution of sodium hydrogen phosphate, and then strong ammonia (.880) equal to about one-third the bulk of the solution, shaking it during the addition. Cork the flask with a rubber stopper. If possible allow to stand overnight after shaking it till precipitation has commenced. If required sooner it may be shaken for fifteen minutes, and allowed to stand not less than one hour. Filter through a 7 cm. ashless paper (preferably not too soft in texture), and wash six or eight times with small quantities of washing ammonia. (See chapter xii.) Dry in a steam oven, detach the precipitate as completely as possible from the paper, ash the paper in a platinum crucible, and then introduce the precipitate. Cover the crucible with a lid, and heat over a Bunsen, first with a flame barely touching the crucible, then gradually increasing the flame until full on. Remove the lid, and continue the ignition till all carbon is burnt away. Cool and weigh as Mg.P.O.

Weight of $Mg_1P_2O_7$ in grammes $\times 101.43 = \text{grains of } MgO \text{ per gallon.}$

Iron, Aluminium, and Manganese.—If the ammonia precipitate obtained from the lime quantity is very small it will in most cases be sufficient to ignite and weigh it, considering it as iron, aluminium, or manganese, or a mixture, according to its colour when precipitated, which is usually a fairly accurate guide. Should it be

considered necessary to estimate each constituent, dissolve the precipitate through the paper with hot dilute hydrochloric acid, and pour it slowly into a boiling solution of pure caustic potash in a nickel dish, making sure that the caustic potash is decidedly more than will be necessary to neutralise the acid. Boil, filter, and wash the precipitate which contains the iron and manganese. Acidify the filtrate with hydrochloric acid, and precipitate the alumina in the boiling solution, in a 5 in. deep form porcelain dish, with the least possible excess of ammonia. Boil, filter, wash, and ignite the precipitate over a blowpipe or Meker burner, and weigh as Al₂O₂.

Weight in grammes \times 280 = grains of Al₂O₃ per gallon.

Dissolve the precipitate of iron and manganese in hydrochloric acid, add bromine water, and reprecipitate with ammonia while boiling in a porcelain dish. Boil, filter, wash, ignite over a blowpipe or Meker burner, and weigh as mixed oxides of iron and manganese.

Weight of precipitate in grammes \times 280 = grains of Fe₂O₃ and Mn₃O₄ per gallon.

Estimate Iron in a separate quantity of water by the colorimetric method as follows. Boil a suitable quantity of water (not exceeding 50 c.c.) for about one minute with three or four drops of hydrochloric acid and two drops of strong nitric acid. (If 50 c.c. of water has been used, evaporate to about 40 c.c.) Cool, add 6 c.c. of potassium sulphocyanide solution (10 per cent.) and 2 c.c. dilute hydrochloric acid, and dilute to 50 c.c. in a Nessler cylinder. Into a similar cylinder put 6 c.c. of potassium sulphocyanide and 2 c.c. dilute hydrochloric acid, and dilute to rather less than 50 c.c. Add, from a burette, Standard Ferric Solution till the colour of the sample quantity is exactly matched, completing the dilution to

50 c.c. when nearly sufficient Ferric solution has been added.

c.c. of Ferric solution \times 7 \div c.c. of water taken = grains of Fe per gallon.

Fe \div 0.7 = grains of Fe₂O₂.

The quantity of water taken should be such as will require not more than about 2 c.c. of Ferric solution, otherwise the colour will be too deep for accurate comparison. A suitable quantity can be decided upon by making a qualitative test on about 10 c.c. in a test tube.

The difference between the mixed Fe_2O_3 and Mn_3O_4 , and the Fe_2O_3 , separately determined = Mn_3O_4 .

Sulphuric Anhydride.—Evaporate 500 c.c. in a 7 in. porcelain dish, acidifying with about eight drops of hydrochloric acid. When reduced to about 40 to 50 c.c. rinse into a 6 oz. conical beaker with hot water. The total volume should not be more than 70 c.c. unless much sulphate is present. Raise to boiling, and add about 5 c.c. barium chloride solution, shaking all the time. Boil for a few seconds, and then add a little more barium chloride to test if precipitation is complete. When the sulphates are all down, boil for a few minutes, and allow to stand on a steam hole for at least two hours. Filter through a 7 cm. paper of fine texture, wash well with nearly boiling water, ignite, and weigh as BaSO₄. If the precipitate is large, it should first be washed several times by decantation, boiling up each time.

Weight of BaSO₄ in grammes \times 48.016 = grains of SO₃ per gallon.

Total Dissolved Solids.—Evaporate 70 c.c. to dryness in a platinum dish on a steam hole, heat in an air oven at 270° Fahr.* till constant in weight. It is usually advisable to heat for about three hours before the first

^{*} If dried at a higher temperature Nitrates may be decomposed.

weighing. Always closely cover the dish while cooling in the desiccator.

Weight of solids in milligrammes = grains per gallon. It is sometimes advisable to ignite the solids very gently after weighing, and weigh the Inorganic Solids.

Chlorine.—Evaporate 70 c.c. in a 3½ in. porcelain dish over a steam hole, till only two or three drops remain. Cool, add one drop of potassium chromate solution, and titrate with Standard Silver Nitrate till the slightest permanent brown tint is obtained, which remains after stirring, and washing down by means of the solution any chlorides which remain on the sides of the dish. Deduct 0.05 c.c. from the observed reading, for excess of silver nitrate used in obtaining the brown tint.

If alkaline sodium salts are present, as indicated by the alkalinity being greater than the total hardness, they may interfere with the titration. In such cases, all but about 2 grains of the alkalinity should be neutralised by the addition of a suitable measured quantity of N/50 Sulphuric Acid before evaporating the water for this determination.

Waters liable to become acid when evaporated, such as those containing iron, should be stirred with a few milligrammes of pure calcium carbonate, evaporated nearly to dryness, filtered, and again evaporated down.

c.c. of Standard Silver Nitrate = grains of Cl per gallon.

If the Chlorine is over 20 grains per gallon, less than 70 c.c. of the sample should be used, whilst if it is particularly high it may be advisable to estimate it gravimetrically.

Alkalinity.—Choose, and reserve for alkalinity determinations, two deep 5 in. porcelain dishes which match each other in colour. Into one, used for purposes of

comparison, measure 0.5 c.c. methyl orange solution with a pipette, and run in 0.4 c.c. N/50 Sulphuric Acid from a 50 c.c. burette, and afterwards refill the burette. Into the other basin measure 70 c.c. of the sample, and add a few drops phenolphthalein solution. If no red colour is produced the whole of the Alkalinity is present as Bicarbonate, and the titration may be conducted with methyl orange as directed below. If a red colour is produced, slowly add N/50 Sulphuric Acid from the burette, the jet being near the surface of the water, stirring with as little agitation as possible. The acid required to destroy the colour completely indicates the alkalinity to Phenolphthalein.

Continue the titration after adding 0.5 c.c. methyl orange solution from a pipette. (Stirring may now be more vigorous.) As soon as the least change from yellow to pink occurs, note the burette reading, and add to the comparison basin 70 c.c. of distilled water plus a further quantity about equal to the volume of acid used in the titration. Continue the titration till the colour of the sample matches that of the blank. As the colour of the blank was produced by 0.4 c.c. of Standard Acid, it follows that 0.4 c.c. excess has been used in the titration, so that 0.4 c.c. must be deducted from the burette reading to obtain the amount required by the water.

N/50 Acid required in c.c. = total Alkalinity in grains per gallon, expressed in terms of Calcium Carbonate.

If there is no alkalinity to Phenolphthalein all the alkalinity is present as *Bi*carbonate.

If the Phenolphthalein Alkalinity is not more than half the Total, on multiplying it by 2 the Alkalinity as Carbonate is obtained, and the difference between the Carbonate and the Total represents Bicarbonate Alkalinity.

If the Phenolphthalein Alkalinity is more than half the Total, the difference between it and the Total Alkalinity, multiplied by 2, equals the Carbonate; and the difference between the Total and the Carbonate is Caustic Alkalinity.

Nitric Anhydride.—If the water does not contain more than about one grain per gallon of chlorine, 70 c.c. may be used for the determination. Where more chlorine is present a smaller quantity of the sample should be taken, such as will contain not much more than 1 mg. of chlorine. In cases where the chlorine is particularly high it is necessary, before commencing the determination of nitric anhydride, to add a solution of a weighed quantity of silver sulphate sufficient to precipitate nearly, but not quite, all the chlorine. After heating till the precipitated silver chloride has thoroughly coagulated, the solution is filtered, and the estimation proceeded with.

Evaporate a suitable quantity of the water* to dryness over a steam hole in a 3½ in. porcelain dish kept specially for the purpose. (If the dish has been used for other work where nitrates are present, such as the determination of chlorine, a high result may be obtained owing to nitrates retained in the glaze.) Waters liable to become acid when evaporated should first be stirred with a few milligrammes of calcium carbonate, evaporated nearly to dryness, filtered, and then evaporated to dryness. Cool, and add from a pipette approximately 2 c.c. of phenol disulphonic acid, thoroughly wetting all the residue in the dish with it, using a glass rod to assist in so doing. When all the residue is seen to have been thoroughly disintegrated, dilute with about 50 c.c. of cold water, add an excess of caustic potash (50 per cent. solution convenient), which

^{*} Do not use the total solids quantity as some of the nitrate may have been decomposed on drying at 270° Fahr.

in the presence of nitrates produces a yellow colour. Dilute with water to 100 c.c. in a measuring flask, and filter if necessary (12½ cm. folded filter). Compare the colour against standards (prepared as below) in 50 c.c. Nessler cylinders, diluting it quantitatively till it exactly matches one of the standards. In order to avoid wasting the standards, it is better to choose one paler than the sample. The sample quantity can be carefully diluted till 50 c.c. matches the chosen standard, and the amount of dilution required noted.

If 50 c.c. of the sample has been used, and 50 c.c. of the yellow solution obtained after treatment and dilution to 100 c.c. requires diluting to 68 c.c. in order to match the 0.05 grain nitrogen standard, then the nitrate present in 50 c.c. of the water is equal in amount to that in 70 c.c. of a water with $\frac{98}{50} \times 0.05 = 0.068$ grain nitrogen. In other words, the sample contains $\frac{7}{4} \times 0.068 = 0.095$ grains of N, or $0.095 \times 3.855 = 0.366$ grain N_2O_5 per gallon.

Owing to the presence of organic matter, the yellow colour is in some cases of a slightly different tint from the standard, but a sufficiently accurate comparison can usually be made. In such cases, if greater accuracy is necessary, the nitrates may be determined by the nitrometer method. (See page 69.)

Some filter papers appreciably affect the colour of the alkaline solution, and the particular brand used for filtering it should be tested in the first place by comparing the colour of the solution after filtration against a portion which has been decanted.

To prepare the nitrate standards, take 20 c.c. of the Standard Potassium Nitrate solution, which will contain 2 mg. of Nitrogen. Evaporate to dryness, treat with 2 c.c. phenol disulphonic acid, dilute, make alkaline

with caustic potash, and dilute to 200 c.c. This will be a 1 grain Nitrogen Standard. Dilute portions of this to make other convenient standards, such as 0.5, 0.2, 0.1, 0.05, 0.04, 0.03, 0.02, 0.01 grain, keeping each in a 100 c.c. stoppered bottle. These standards appear to keep indefinitely, but as the caustic potash attacks the glass they will occasionally need filtering, and it is wiser to make up an entirely fresh set from time to time.

Nitrates by the Nitrometer Method.—For this purpose evaporate 250 c.c. (less if much nitrate is present) in a 6 inch porcelain dish till only about two or three cubic centimetres remain, filter through a 51 cm. paper into a 3 inch porcelain dish, washing the filter two or three times with small quantities of water. Evaporate to about 1 c.c. and rinse into a Lunge's nitrometer (filled with mercury), making the volume of solution in the nitrometer just 3 c.c. Run in strong sulphuric acid (1.84) very carefully, to make the total volume 7.5 c.c. Expel the carbonic acid which will usually be evolved. Shake thoroughly and vigorously, so that the mercury mixes with the acid solution, and until no more gas is evolved when the solution is further shaken. Pour on to the mercury in the levelling tube a mixture of 3 c.c. of distilled water to which strong sulphuric acid has been added to make a total volume of 7.5 c.c. When the liberated gas is cold, adjust the level of the mercury in the two tubes, and read off the volume of Nitric Oxide (NO). Correct the volume of gas for temperature and pressure.

Corrected volume of gas in c.c. from 250 c.c. water \times 0.175 = grains of N per gallon.

Nitrogen $\times 3.855 = \text{Nitric Anhydride (N}_2\text{O}_5).$

In order to avoid the necessity of correcting the volume of NO for temperature and pressure, it is a good plan to keep a second nitrometer, with the stop-cock specially well greased and tied in, charged with the NO liberated from 0·103 gramme of pure potassium nitrate, which will be equivalent to 4 grains of Nitrogen per gallon when working on 250 c.c. of water. Keep this standard beside the other nitrometer, and take a reading whenever a sample quantity is being read off.

c.c. of NO from 250 c.c. of the sample $\times 4 \div$ c.c. of NO in the Standard tube = grains of N per gallon.

Ammonia should be tested for in every sample, by adding Nessler solution. If more than a faint yellow colour is produced the ammonia should be estimated.

To a suitable quantity of water (see below) add a few milligrammes of sodium carbonate, and a drop or two of 50 per cent. caustic soda, in order to precipitate the hardness. Filter if necessary, and measure out a suitable quantity into a 50 c.c. Nessler cylinder by means of a pipette, and dilute to the mark with water. Add 2 c.c. of Nessler solution and stir. In an exactly similar cylinder have nearly 50 c.c. of distilled water, add 2 c.c. of Nessler solution, and then add Standard Ammonium Chloride solution from a burette in suitable small quantities, until, after standing two or three minutes, the colour matches the sample quantity. When nearly sufficient Standard Ammonium Chloride has been added, the comparison quantity should be diluted with water, if necessary, till its volume is equal to that of the sample quantity.

c.c. of Ammonium Chloride solution required $\times 3.5 \div$ c.c. of water taken = grains of NH₂ per gallon.

The quantity of water used should not exceed 50 c.c. for this determination, and should be such as will require not more than about 2 c.c. of Standard Ammonium Chloride to match the colour.

Oxygen.—It is sometimes desirable to determine the amount of oxygen in solution in water. If possible the

test should be carried out, up to the point of titrating, as soon as the sample has been obtained; otherwise the sample should be kept as cool as possible, and in a wellfilled stoppered bottle, and the determination commenced as early as possible.

To 250 c.c. of water in a stoppered flask or bottle add about 2 c.c. each of manganous sulphate solution, and potassium iodide-sodium hydrate solution, each solution being added from a pipette dipping slightly below the surface of the water. Stopper, and gently mix. Add about 2 c.c. dilute sulphuric acid, and mix thoroughly. After this the estimation may be continued when convenient. Titrate with N/40 Sodium Thiosulphate solution, adding a little starch solution towards the end of the titration. The Thiosulphate solution should be standardised by titrating with it 10 c.c. of accurate N/40 Potassium Bichromate, after adding 3 c.c. of potassium iodide solution, and 3 c.c. dilute sulphuric acid, starch solution being added when most of the liberated iodine has been decolorised. Care should be taken that the blue colour remaining in the solution due to the chromium salts is not confused with the blue starch iodide.

True N/40 Thiosulphate in c.c. \times 0.056 = grains of Oxygen per gallon.

Grains of Oxygen per gallon \times 9.964 = c.c. of Oxygen per litre.

Hardness by Soap Test.—The Standard Soap Solution used for this test may be either Clark's or Wanklyn's. If Clark's solution is used, 50 c.c. of water is taken. If Wanklyn's solution is used, 70 c.c. of water will be required.

In either case the required quantity of water is measured into a stoppered bottle having a capacity of about 200 to 250 c.c. The Soap Solution is then run in about 1 c.c. at

a time, stoppering and shaking the bottle between each addition, until signs of a lather are noticed. Smaller quantities of the soap are then added, with shaking, till a good lather is formed, which remains unbroken after standing for five minutes. It is better to lay the bottle on its side while waiting. In the presence of magnesia a false lather may be produced before the end point is reached, and this is sometimes mistaken for the real lather unless care is used. If there is any doubt about it, a reading of the burette should be taken, and another 0.5 c.c. of soap solution added and shaken. If the lather is the true one it will still remain, but a false one will probably have entirely disappeared. A further 0.5 c.c. may be added if there is still a doubt. If the lather disappears continue the titration.

In the case of Clark's solution, the Hardness corresponding to the number of cubic centimetres of soap solution used must be obtained by reference to "Clark's Table of Hardnesses." (See page 97.) When Wanklyn's solution is used, 1 c.c. is deducted from the burette reading, and the remainder represents degrees of hardness.

Whichever solution is used, waters having more than 14 degrees of hardness must be diluted before testing, otherwise the results will be unreliable. Thus, if a water contains, say, 20 degrees of hardness, 25 c.c. may be diluted to 50 c.c. for the Clark test, and the figure for the hardness corresponding to the amount of soap solution used multiplied by 2 to ascertain the hardness of the original water. Similarly, if a water of 20 degrees of hardness is to be tested by the Wanklyn method, 50 c.c. can be diluted to 100 c.c., and 70 c.c. titrated. One cubic centimetre will then be deducted from the observed burette reading, and the remainder multiplied by 2, in order to obtain the hardness of the original water.

Calculation of Results.—It is impossible to say with certainty in what combinations the various bases and acid radicles found by analysis really exist. In all probability variations occur with changes of temperature and concentration, and any attempt to separate the various constituents is, therefore, rendered useless, as boiling and evaporation would be necessary, and the combinations thus materially changed. As it is desirable to have some idea as to what salts are likely to be present, or to be formed under certain conditions, some definite system must be adopted for the allocation of the acids to the various bases. When solutions of different salts are mixed, there is a tendency for the least soluble salts to be formed, and this may be taken as the best basis for the purpose of calculating the probable composition of a water.

The following instructions are given as a guide, but variations may at times be necessary, and must be made at the discretion of the analyst:—

Iron, Aluminium, Manganese, and Ammonia are probably nearly always present as Sulphates when actually in solution, and should, therefore, be usually first calculated as such.

All the Lime, or as much as possible (dependent on the amount of Alkalinity), should then be calculated to Calcium Carbonate.

Any remaining Lime, or as much as possible, to Calcium Sulphate.

Any remaining Lime, or as much as possible, to Calcium Nitrate.

Any remaining Lime, or as much as possible, to Calcium Chloride.

If any Alkalinity remains after calculating Calcium Carbonate, all the Magnesia, or as much as possible, should be calculated to Magnesium Carbonate.

Any remaining Magnesia, or as much as possible, to Magnesium Sulphate.

Any remaining Magnesia, or as much as possible, to Magnesium Nitrate.

Any remaining Magnesia, to Magnesium Chloride.

Any remaining Alkalinity or Acid Radicles may be calculated as Sodium Salts.

Silica may be expressed as such, or calculated as Sodium Silicate.

The difference between the Total Solids and the sum of the calculated constituents may be expressed as "Water not expelled at 270° Fahr., Organic Matter, etc." In some cases it may be mainly Organic Matter, in which case it will readily be noticed when the organic matter is being charred before the *lime* quantity is redissolved after evaporating to dryness.

Where Ammonium salts are present, the sum of the calculated constituents may exceed the estimated Total Solids, owing to the fact that all, or a portion of, the Ammonium salts will be expelled while the solids are drying.

Hardness is the sum of the Lime and Magnesia expressed in terms of Calcium Carbonate. If Iron, Aluminium, or Manganese are present they must also be calculated to Calcium Carbonate, and included in the Hardness, as they also have soap-destroying properties, but it is as well, in order to avoid any misunderstanding, to state "Hardness, including Iron, Aluminium, or Manganese."

"Scale-forming matter" may also be given, and should represent the Magnesia expressed as Magnesium Hydrate, plus Calcium Carbonate, Calcium Sulphate, and Silica. Iron, Aluminium, and Manganese should be included, if present, expressed as Oxides. Scale-forming matter may well be expressed in grains per gallon, and also in pounds per 1000 gallons, the latter being one-seventh the former.

Calculation of Chemicals required for Softening. Lime.—Calculate Lime equivalent to:—

- (1) The Total Alkalinity (Alkalinity \times 0.56).
- (2) The Total Magnesia (MgO \times 1·39).
- (3) The Iron, Aluminium, and Manganese if present.

Add to the sum of these, Lime equivalent to the free CO₂ if it has been estimated; or if it has not been determined, allow 1 grain of Lime per gallon, this being about equivalent to the average free CO₂. Divide the quantity of Lime thus calculated by 7 to bring it to pounds per 1000 gallons, and then divide by 0.9 to obtain pounds of 90% Lime per 1000 gallons. (Best Buxton Hard Lime is usually considered to contain about 90% of Caustic Lime.)

Soda Ash (Alkali 58%).—Deduct the Total Alkalinity from the Hardness, and multiply by 1.08. This gives grains of Sodium Carbonate of 98% quality per gallon. Divide by 7 to bring it to pounds per 1000 gallons.

Alkali 58% is the usual trade description of Soda Ash containing about 58% Na₂O, or 98% Na₂CO₂.

If the Alkalinity exceeds the Hardness, no soda ash is required, as sodium carbonate is already present in the water. If it is necessary to remove sodium carbonate from a water, Calcium Chloride or Aluminoferric may be used, equivalent in quantity to the sodium carbonate present.

Calculation of Chemicals for the Treatment of Water when there is no Softening Plant.

(a) Deduct the Total Alkalinity from the Hardness, multiply by 1.08 and divide by 7. This gives the equivalent of Soda Ash in pounds per 1000 gallons.

- (b) If the Alkalinity exceeds, or is not much less than half the Hardness due to Lime (total $CaO \times 1.784$), only Caustic Soda will be required, in which case the Soda Ash calculated in paragraph (a) must be multiplied by 0.755 to obtain 98% Caustic Soda, and this alone should be used for the treatment.
- (c) If the Alkalinity is decidedly less than half the Hardness due to Lime, some Soda Ash will be needed. Deduct twice the Alkalinity from the Total Lime Hardness, multiply by 1.08 and divide by 7.

This will give the Soda Ash, in pounds, required for the treatment of 1000 gallons of water. Deduct this from the Soda Ash obtained in paragraph (a), and multiply the remainder by 0.755, to ascertain the Caustic Soda necessary for 1000 gallons of water. A mixture of Caustic Soda and Soda Ash is used in this case.

CHAPTER IX

ANALYSIS OF SCALE

As it is sometimes desirable to know the composition of the scale formed in boilers, the following brief description of a method of analysis may be useful:—

About 20 grammes of an average sample should be chosen, ground finely, and well mixed.

Water.—Weigh out 1 gramme into a platinum dish, dry at 300° Fahr. in an air oven till constant in weight.

Organic Matter.—Heat the quantity used for water determination to faintest redness, till all organic matter is completely burnt, and weigh. The loss in weight will be due to organic matter (including oil); and combined water, if any, not expelled at 300° Fahr.

General Analysis.—Ignite 2 grammes very gently in a platinum dish to burn off organic matter. Cool, transfer to a beaker, and add a little bromine water to oxidise sulphides formed by the reduction of sulphates, and any ferrous salts. Cover the beaker, add hydrochloric acid, and boil till as much as possible of the scale has dissolved. Evaporate to dryness on a hot plate, and bake gently for half an hour. Cool, add 10 c.c. hydrochloric acid, heat for a short time, add about 100 c.c. of water, and heat till only silica remains undissolved. Filter into a 500 c.c. measuring flask, wash, dry, and ignite the silica (= Silica on 2 grammes).

Dilute the filtrate to 500 c.c., take 250 c.c. and estimate Sulphates by evaporating to about 70 c.c., rinsing into a 6 oz. conical beaker, and precipitating with barium chloride as in water analysis (= Sulphates on 1 gramme).

Transfer 100 c.c. of the diluted filtrate from the silica to a 5 in. deep form porcelain basin, make just alkaline with ammonia, boil, and filter. Ignite and weigh the precipitate; or separate iron, aluminium, and manganese as in water analysis (= Iron, etc., on 0.4 gramme).

Precipitate Lime in the filtrate from the ammonia precipitate, with ammonium oxalate added 2 c.c. at a time till no further precipitate forms, filter, ignite, and weigh (= Lime on 0.4 gramme).

Slightly acidify the filtrate from the lime with hydrochloric acid, evaporate to about 70 c.c., make alkaline with ammonia, and precipitate Magnesia with sodium phosphate as in water analysis, filter, ignite, and weigh (= Magnesia on 0.4 gramme).

Carbonates.—It is not usually necessary to determine these, but if required the estimation may be carried out as follows:—

Place 1 gramme of the powdered sample in a flask of about 300 c.c. capacity, fitted with a cork having two holes. Through one hole insert a funnel with a stop-cock, and having a neck so that a purifying train may be connected through the funnel to the flask. The stem of the funnel should reach nearly to the bottom of the flask, and should be drawn out to a small diameter at the end, and turned up for about ½ in. The other hole in the cork is fitted with a short glass tube which is connected to the following series:—

⁽¹⁾ Dry, empty "U" tube.

- (2) "U" tube of pumice soaked in concentrated sulphuric acid.
- (3) Another "U" tube of pumice and sulphuric acid.
- (4) "U" tube of pumice which has been soaked in a solution of copper sulphate, dried, and heated to render the copper sulphate anhydrous.
- (5) Another "U" tube of sulphuric acid and pumice.
- (6) Two "U" tubes tied together and connected in series, the first filled with soda lime, and the second with pumice and sulphuric acid. These are the absorption tubes and should be weighed together.

In addition to these, a wash-bottle of strong caustic soda solution, connected to a "U" tube of soda lime, should be provided for the preliminary purification of the air required for driving the carbonic acid forward, and it must have a rubber tube by which the "U" tube can be connected to the top of the funnel in the evolution flask when necessary.

Put sufficient water in the flask to cover the sample, and insert the cork. Connect up to the long purifying train detailed above. Put 10 c.c. of hydrochloric acid in the stoppered funnel.

Commence by passing a current of air (about 1 litre per hour) through the preliminary purifying train.

Run the acid gradually from the funnel into the flask, but leave sufficient in the turned-up end of the stem to form a seal. When the effervescence has practically ceased, heat the contents of the flask, and boil gently for two minutes. Now connect up the preliminary purifying train to the funnel and open the stop-cock, so that the

current of purified air passes through the flask, and thus displaces the remaining carbonic acid. Turn out the flame under the flask. Allow the air to pass through the apparatus for half an hour, and then weigh the absorption tubes. The increase in weight $= CO_2$ on 1 gramme.

Calculation of Results.—Calculate all the Sulphate to Calcium Sulphate. Then, if Carbonic Acid has been estimated, calculate it all (if possible) to Calcium Carbonate.

Should any Carbonic Acid remain, it must be calculated to Magnesium Carbonate.

If there is insufficient Carbonic Acid for the Lime remaining after calculating Calcium Sulphate, the excess Lime must be present as Calcium Hydrate (Caustic Lime).

Unless it has been necessary to calculate Magnesium Carbonate, the whole of the Magnesia should be expressed as Magnesium Hydrate.

If Carbonic Acid has not been estimated, any Lime left after calculating Calcium Sulphate should be expressed as Calcium Carbonate, and all the Magnesia as Hydrate.

If the sum of the calculated constituents, plus the Water and Organic Matter, exceeds 100 per cent., a sufficient quantity of the Magnesia must be expressed as Magnesium Oxide (instead of Hydrate) to reduce the total to 100 per cent.

CHAPTER X

CONTROL TESTS FOR WATER SOFTENING

SOFTENING treatment should be carefully controlled by regular testing of the softened water. Tests ought to be made at least once a day, and where the water is liable to frequent changes in composition more frequent tests are necessary.

At the commencement, and from time to time afterwards, the plant should be carefully examined to ascertain whether it is working uniformly. In the case of tipping-buckets the number of tips per minute should be counted for several minutes, at a time when the demand for water is steady, and notice taken whether the buckets are filled to the same level each time.

All moving parts should be observed to detect any signs of sticking.

With plants which deliver the reagents in the form of solutions of constant strength, the strength of the solutions should be tested at intervals.

Any measuring devices should be cleaned, and kept clean.

The plant having been found apparently working satisfactorily, tests of the water, as it enters and leaves the plant should be made, at intervals, several times during the day. Should the incoming water be found uniform in composition, but the treated water variable, the cause must be investigated and removed.

In most cases it is only necessary to determine the Hardness and Alkalinity. The method for Alkalinity described in chapter viii is quite simple, and can readily be made by any one, but it should be carried through carefully, especially the first part of the test where phenolphthalein is used as indicator.

Various methods have been devised for the determination of Hardness, but the soap test as described in chapter viii, originally devised by Dr. Clark, is the most useful and convenient; and if carried out carefully usually gives sufficiently accurate results for the daily control of softening treatment. Methods necessitating boiling and evaporation are inconvenient, except in a chemical laboratory, and the results are not usually any more reliable than those obtained by the soap test, and some are decidedly unreliable.

Having made the tests, we must now consider what results are to be aimed at for a boiler feed water, and how they can be attained.

In the first place, the Hardness should be reduced as low as possible. It is frequently stated that this is undesirable, and that water for boiler feeding purposes should have at least 5 degrees of hardness. Experience does not confirm this, however, provided that other conditions are fulfilled. This mistaken idea has probably arisen partly owing to the fact that many of the naturally soft waters are more or less corrosive, and partly to the effects of some waters softened to a fairly low degree, but not fulfilling other conditions of efficient softening; or to softened waters used without sufficient regard to the effect of undue concentration, in boilers, of the soluble constituents.

Secondly, the Magnesia should be removed as completely as possible. Whereas Calcium Carbonate, which

is probably the salt most easily removed by softening treatment, tends to neutralise the corrosive effect of other salts, Magnesium compounds are always apt to set up corrosive action. It will be clearly understood, therefore, that if imperfect softening results in the removal of most of the Calcium Carbonate while leaving the Magnesium salts, the corrosive tendencies of the latter have freer play; and whereas a water may have been used untreated without causing corrosion, inefficient softening may lead to wasting of the boiler plates, and the softening plant will be unjustly condemned.

The third important condition is that there should be a slight excess of Alkaline Sodium Salts in the treated water, unless other circumstances render them undesirable. Occasionally a portion of the softened water may be required for purposes other than boiler feeding, purposes for which an excess of soda would be harmful. In such cases it is better, if possible, to treat the water as for boiler feeding, and afterwards neutralise the portion required for other uses. It is also sometimes claimed that the steam from boilers fed with water treated with soda is objectionable for certain purposes, such as cooking. This can only be the case where either an undue accumulation of soda in the boiler is allowed, or where priming results in the carrying forward of the alkaline water with the steam.

To fulfil all the foregoing conditions, the Total Alkalinity must be slightly higher than the Hardness, and the Alkalinity of the water to Phenolphthalein must be slightly more than half the Total Alkalinity

If the Total Alkalinity is less than the Hardness, the proportion of Soda Ash requires increasing, while if it exceeds the Hardness by more than 0.5 degree it is usually desirable to reduce the Soda Ash. As every degree of Hardness or Alkalinity is equivalent to approximately 2½ ounces of Soda Ash per 1000 gallons, the proportion of Soda Ash must be increased or decreased by this amount for every degree difference between them, always allowing 1 ounce more Soda Ash per 1000 gallons for the desirable excess.

If the Alkalinity to Phenolphthalein exceeds half the Total Alkalinity, the presence of Caustic Alkalinity is indicated, and, as Magnesium Hydrate is almost insoluble in water, it follows that this condition is required for the effective removal of Magnesia. As a rule about 0.5 grain of Caustic Alkalinity is sufficient for the purpose, though with some waters more is desirable. If the N/50acid required for the Alkalinity to Phenolphthalein exceeds half that required for the Total Alkalinity by 1 c.c., 2 grains of Caustic Alkalinity is indicated, equivalent to 1.12 grains of pure Lime per gallon, or approximately 3 ounces of commercial Quick-lime of 90 per cent. quality per 1000 gallons; and the proportion of Lime must therefore be increased or decreased by this amount for every 1 c.c. difference between the Alkalinity to Phenolphthalein and half the Total Alkalinity, I ounce more Lime per 1000 gallons being allowed for desirable excess.

The foregoing instructions are suitable for general guidance, but some waters may be found to require special conditions in order to obtain the best results. In such cases it is usually greater excess of reagents which is called for.

Having arrived at what appears to be satisfactory treatment, it is very desirable that a sample should be analysed for Lime, Magnesia, and Alkalinity in a laboratory, in order to ascertain whether Magnesia is being effectively removed, and also to act as a check on the soap test, and the accuracy of the standard solutions used in the

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daily testing. It is also advisable to have such a check carried out periodically, say once a month.

The standard solutions should also be tested occasionally, especially the soap solution, which, being made with alcohol, is very liable to evaporate and so become stronger. A Standard Sodium Carbonate solution of one-three-hundred-and-fiftieth normal strength is useful for checking the Standard Acid, 70 c.c. of this strength requiring 10 c.c. of Standard Acid, and the test can be carried out with the same apparatus, and under the same conditions, as the water samples.

For checking the Standard Soap solution, a Standard Hard Water is needed. This may conveniently be of 14 degrees Hardness, and will be used exactly as in testing water samples.

If either solution is found to be appreciably too strong, it may be carefully diluted (using water for the acid, or alcohol for the soap) till correct; or a factor may be made by which the volume of solution used in the titration may be corrected.

For works use it is usually considered better to have cylinders for the measurement of the water required for the tests, in preference to the more fragile pipettes.

CHAPTER XI

SAMPLING

THOUGH it is a simple matter to collect a sample of water, the importance of fair sampling justifies a few remarks on the subject.

The most suitable bottles for the purpose are Winchester Quarts. They should have glass stoppers for preference, but if stoppered bottles cannot be obtained, clean sound corks may be used. Screw-stoppered bottles are unsuitable as they have usually been used for ammonia, which permeates the screw stoppers and cannot be entirely removed by washing.

If possible, clear glass bottles should be obtained, so that the appearance of the sample can be judged without the necessity of transferring to another vessel.

The sample bottles, after thorough cleansing, should be rinsed out three times with the water to be sampled.

Whenever possible, samples should be collected directly into the bottles; but if this is impossible, glass or earthenware vessels should be used in preference to those made of metal.

Bottles should always be filled to within an inch of the cork or stopper, but a little air space is essential, otherwise the bottle may burst.

Samples from ponds, tanks, or rivers should be taken by plunging the bottle (or other vessel) two inches or more below the surface of the water, in order to avoid any surface contamination.

When a sample is to be obtained from a tap, or a pump which has been standing, sufficient water should first be run to waste to avoid taking water which has been standing in the pipes.

If an estimation of dissolved gases is required, the sample should be collected with as little agitation as possible, the bottle filled as full as consistent with safety, and the sample kept as cool as possible until the determination has been made.

Boiler samples should be drawn from a water-gauge cock, after first flushing out. Care should be taken that the steam cock is closed, otherwise the sample will be diluted with condensed steam. In the case of boiler samples, a clean bucket may be used for collecting the hot water, which should then be poured into an earthenware vessel to cool somewhat before it is transferred to the bottle.

Every sample should be labelled with full particulars as soon as obtained, and the stopper should be covered with a piece of calico or other material, and securely tied down.

Winchester quart bottles can usually be sent by rail, per passenger train, without packing, with an addressed tag label tied to the neck. Except at holiday times samples thus sent usually reach their destination in safety. They are safer without packing than if badly packed.

If bottles are to be packed, the box should be large enough to allow plenty of clearance all round for wood-fibre or straw packing. No wedges should be used to hold the bottles in position, as this almost invariably results in breakage. Sawdust is not a good packing material, as it settles down into too solid a mass, and the bottles may break if the package receives a sudden jar.

CHAPTER XII

SOLUTIONS

REAGENTS

Hydrochloric Acid, sp. gr. 1·11. HCl (1·16) 1500 c.c., Water 900 c.c.

Nitric Acid, sp. gr. 1.2. HNO₃ (1.42) 800 c.c., Water 1280 c.c.

Ammonia, sp. gr. 0.95. Ammonia (.880) 1000 c.c., Water 1500 c.c.

Washing Ammonia.

Ammonia (.880) 1 part, Water 3 parts.

Barium Chloride

10 per cent. solution.

Ammonium Oxalate.

3.5 per cent. solution.

Sodium Phosphate.

Saturated solution of Disodium Hydrogen Phosphate.

Methyl Orange.

0.15 gramme per litre.

Phenolphthalein.

3 per cent. solution in rectified spirit, decolorised if necessary by shaking with a little animal charcoal, filtered, and then neutralised by shaking with a little quicklime, and filtered.

Phenol Disulphonic Acid.

Dissolve 25 grammes of Phenol in 150 c.c. of concentrated sulphuric acid (1.84) and 75 c.c. furning sulphuric acid (13 per cent. SO₃), and heat for 1 hour at 100° C.

Manganous Sulphote.

48 per cent. solution.

Sodium Hydrate and Potassium Iodide Solution.
360 grammes NaOH and 100 grammes KI dissolved in water and diluted to 1000 c.c.

Nessler Solution.

Dissolve 62.5 grammes of KI in about 250 c.c. of distilled water. Reserve about 10 c.c. of this, and gradually add to the main portion a cold saturated solution of mercuric chloride until a slight permanent precipitate remains after shaking. Add potassium iodide and mercuric chloride solutions alternately till the former is nearly all used up, and a slight permanent precipitate remains. Add a cold solution of 150 grammes of caustic potash in 150 c.c. of water, and dilute to 1000 c.c. Keep the solution in a rubbercorked bottle, decanting a portion of the clear solution into a smaller bottle from time to time as required.

Potassium Sulphocyanide.

10 per cent. solution.

Bromine Water.

Saturated solution in water.

Potassium Iodide.

10 per cent. solution.

Potassium Chromate.

10 per cent. solution, free from chlorides.

STANDARD SOLUTIONS

Sulphuric Acid, N/50.

Dilute 10 c.c. of Normal Sulphuric Acid to 500 c.c.

Sodium Carbonate, N/350.

First make N/50 by diluting 10 c.c. of Normal Sodium Carbonate to 500 c.c.; and then dilute 71.4 c.c. of this to 500 c.c. (measure 70 c.c. with a pipette, and 1.4 c.c. from a burette).

Sodium Carbonate for CO_2 Determination.

1.723 grammes of anhydrous Sodium Carbonate per 500 c.c.

Silver Nitrate.

4.7944 grammes per litre (1 c.c. = .001 gramme . Chlorine).

Ammonium Chloride.

0.1568 gramme per litre (1 c.c. = 0.00005 gramme of NH₃).

Ferric Sulphate.

0.7 gramme of crystallised Ferrous Ammonium Sulphate and 5 c.c. dilute sulphuric acid, dissolved in water, made just pink with potassium permanganate, and diluted to 1000 c.c. (1 c.c. = $\cdot 0001$ gramme Fe).

Hard Water (14 degrees).

Dissolve 0.2 gramme of Calcite in dilute hydrochloric acid, and evaporate to dryness in a platinum dish. Add a little water and evaporate to dryness again, repeating this several times to remove all trace of acid. Dissolve in water, and dilute to 1000 c.c.

Clark's Soap Solution.

Triturate 150 parts of Lead Plaster (Plumbi Emplast, B.P.) in a mortar with 40 parts of anhydrous Potassium Carbonate. When well mixed add a little methylated spirit, and again triturate until a smooth cream is formed. Add more spirit, stir, allow to stand for a short time, and filter. Keep this as a stock solution, diluting portion from time to time as required. Dilute with 2 parts of methylated spirit and 1 part water till 50 c.c. of Standard Hard Water requires 14.25 c.c. of the Soap Solution to produce a permanent lather.

Sodium Thiosulphate.

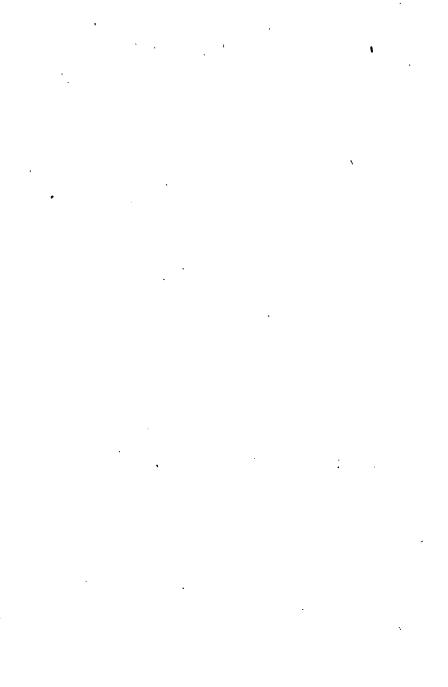
6.2 grammes per litre, standardised against N/40 Potassium Bichromate.

Potassium Bichromate, N/40.

Heat powdered Potassium Bichromate over a very small flame till the colour just changes from orange to brown. Cool in a desiccator, and weigh out 0.6129 grammes. Dissolve in water and dilute to 500 c.c.

Potassium Nitrate.

0.3609 grammes per 500 c.c. (10 c.c. = .001 grm. N).



APPENDIX

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LIST OF FACTORS

Given	Wanted	Factor	Given	Wanted	Factor
Al ₂ O ₃	3CaO	1.64589	CaSO ₄	Na ₂ CO ₃	·77870
Al_2O_8	3SO ₃	2.85008	$Ca(NO_3)_2$	Na ₂ CO ₃	·64602
BaSO ₄	SO ₃	84297	CaCl ₂	Na ₂ CO ₃	∙95509
$ \begin{array}{c} \mathbf{BaSO_4} \\ \mathbf{grms. per} \\ \mathbf{500 c.c.} \end{array} $	SO ₃ grs. per gal.	48.016	CO ₂	CaO NaCl	1.64862
CaO (CaCO ₃	1.78482	$\mathbf{Fe_2}$ $\mathbf{Fe_2O_3}$	Fe ₂ O ₃ 2CaO	1·42980 ·70228
mgrms. per 250 c.c.	grs. per gal.	.5	Fe_2O_3 Fe_2O_3	2FeSO ₄ 2SO ₃	1·90256 1·00276
CaO	Na ₂ CO ₃	1.89058	Fe ₂ O ₃	2CaCO ₃	1.25344
CaO	CO ₂	·7848	Fe ₂ O ₃	2FeCO ₃	1.45096
CaO	SO ₃	1.42788	Fe ₂ O ₃	2CaCO	87482
CaO	CaCl,	1.97946	Fe ₂ O ₃	2CaO	·49015
CaO	Cl.	1.26485	Mn ₃ O ₄	3MnSO ₄	1.97985
CaO	N ₂ O ₅	1.92652	Mn ₃ O ₄	3SO ₃	1.04978
CaO	2NaOH	1.42708	Mg P O,	2MgO	-86225
CaO	MgO	·71910	Mg ₂ P ₂ O ₇)	MgO)	
CaO	MgCO ₂	1.50388	grms. per	grs. per	101.480
CaCO.	CaO	·56028	250 c.c.	gal.	
CaCO.	MgO	·40290	MgO	CaO	1.39068
CaCO ₃	MgCO,	-84262	MgO	CaCO ₈	2.48202
CaCO.	Na ₂ CO ₃	1.05926	MgO	MgCO ₃	2.09189
CaCO.	2NaOH	·79956	MgO	MgCl ₂	2.86210
CaCO ₃	H ₂ SO ₄	·98002	MgO	Cl ₂	1.75898

LIST OF FACTORS—continued

Given	Wanted	Factor	Given	Wanted	Factor
MgO	SO ₃	1.98562	2NH ₃	SO ₃	2.85001
MgO	N ₂ O ₅	2.67907	2NH ₃	$(NH_4)_2SO_4$	3.87888
MgO	Mg(OH)	1.44683	SiO ₂	Na ₂ O	1.02819
MgO	Na ₂ CO ₃	2.62909	Na ₂ CO ₃	2NaOH	·75482
MgO	2NaOH	1.98452	Na ₂ CO ₃	CaCl ₂	1.04703
MgCO ₈	CaCOa	1.18690	Na ₂ CO ₃	CaO	· 52 894
MgSO ₄	Na ₂ CO ₃	·880 5 9	Na ₂ CO ₃	BaCO _a	1.86194
Mg(NO ₃),	Na ₂ CO ₃	·71461	SO ₃	Na ₂ O	·77442
MgCl ₂	Na ₂ CO ₃	1.11303	SO ₃	MgO	·50362
N ₂	N ₂ O ₅	3.85510	SO _a	CaO	·70026
N ₂ O ₅	Na ₂ O	·57897	H ₂ SO ₄	SO ₃	·81636
N ₂ O ₅	MgO	·37326	H ₂ SO ₄	Na ₂ CO ₃	1.08085
N_8O_5	CaO	·51907	H ₂ SO ₄	CaO	.57170

ATOMIC WEIGHTS

(International, 1918)

Aluminium	•	$27 \cdot 1$	Manganese	•	54 ·93
Barium .		137.37	Nitrogen .		14.01
Calcium .		40.07	Oxygen .		16.00
Carbon .		12.005	Potassium		39.10
Chlorine .		$35 \cdot 46$	Silicon .		28.3
Hydrogen	•	1.008	Silver .		107.88
Iron .		55.84	Sodium .		28.00
Magnesium		24.82	Sulphur .	•	82.06

TABLE OF HARDNESSES

CLARK'S TABLE OF HARDNESSES (in degrees)

ပ်	0.0	0.1	0.2	0.8	0.4	0.5	9.0	2.0	8.0	6.0
0		ı	1	1	1	1	1	0.00	0-11	0.23
-	0.88	0.44	0.55	29.0	9.4	0.89	1.00	1.09	1.18	1.27
69	1.86	1.45	1.54	1.64	1.73	1.88	1.98	2.01	5 ·09	2.18
8	2.28	2.87	2.46	2.55	2.64	2.78	2.83	2.91	8.00	8·10
4	8.20	8.80	8.40	8.50	8.60	8.70	8.80	8.90	4.00	4.10
20	4.20	4.80	4.40	4.50	4.60	4.70	4.80	4.90	2.00	5.10
9	2.50	2.80	2.40	2.20	2.60	5.70	2.80	2.80	9.00	6.10
4	6.20	6.30	6.40	6.50	9.90	6.70	6 ·80	06.9	4.00	7.11
œ	7.21	7.82	7.42	7.58	7.63	7.74	7.84	7.94	8.05	8·16
6	8.26	8-87	8.48	8.58	8.69	8.79	8.90	9.00	9-11	9.31
10	9.82	9.42	9.58	89.6	9.74	9.84	9.92	10.06	10.18	10.28
11	10.89	10.50	10.01	10.72	10.88	10.94	11.05	11.17	11.28	11.89
12	11.50	11.61	11.72	11.88	11.94	12.05	12.17	12.28	12.89	12.50
18	12.61	12.72	12.88	12.94	13.06	18.17	18.28	18.89	18.50	18.61
14	18.72	13.88	18.94	14.06	14.17	14.28	14.89	14.50	14.61	14.72
15	14.83	14.95	15.06	15.18	15.29	15.41	15.58	15.65	15.78	15.88
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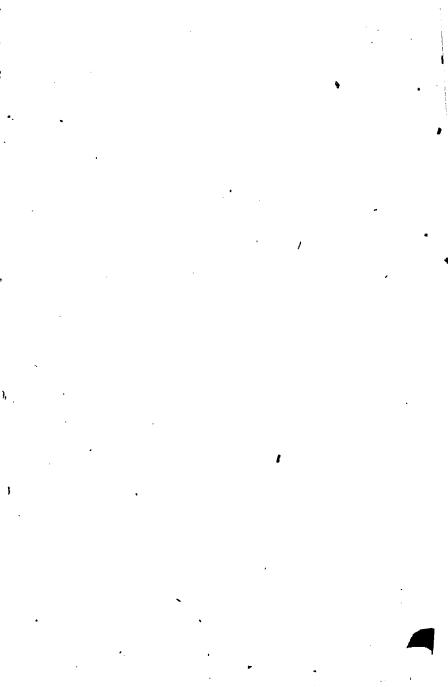
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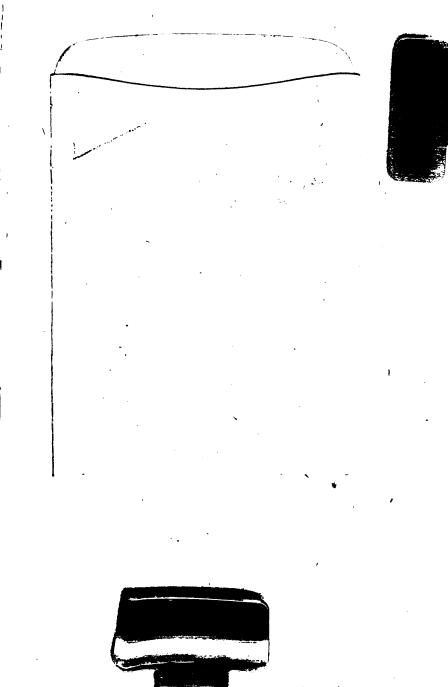


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